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**THE
INTERNATIONAL SERIES
OF
MONOGRAPHS ON PHYSICS**

GENERAL EDITORS

**†R. H. FOWLER, P. KAPITZA
N. F. MOTT, E. C. BULLARD**

THE INTERNATIONAL SERIES OF MONOGRAPHS ON PHYSICS

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PREFACE TO SECOND EDITION

SINCE the publication of the first edition of this book, the most important new developments in the theory of atomic collisions have been its applications to nuclear physics. Although no new techniques have been introduced for dealing with extra-nuclear collision phenomena, in this field too, much progress has been made. The stage has now been reached where it is necessary in such branches of research as astrophysics, solar physics, and in the physics of the upper atmosphere, to have available reliable information on the rates of various collision processes. It was felt that a review of the available information about these processes, together with an up-to-date discussion of nuclear collisions, would lead to a book of undue length. The plan has therefore been followed in this second edition of describing primarily the new work on nuclear collisions and generally bringing the theory up to date. More detail has been given about relativistic scattering in which radiation is not involved and, to clarify certain arguments, some discussion has been given of the validity of different approximations and some hints on numerical procedure. No attempt has been made to enlarge the discussion of applications of the technique to atomic, as against nuclear, collisions, except where a further direct test of some aspect of the theory has become possible. The chapter on collisions of electrons with molecules has been omitted.

To meet the growing need for an account of the information, available from both experimental and theoretical sources, about the rates of various atomic, as distinct from nuclear, collision processes, a second book, 'Electronic and Ionic Impact Phenomena', which is not primarily theoretical, and includes a description of experimental methods, is in preparation. It is being written, in collaboration with Dr. E. H. S. Burhop, by the one of us (H. S. W. M.) who has been largely responsible for the preparation of this second edition. References to the new book are included in this edition whenever it is necessary to call attention to the existence of a body of information on a particular aspect of the subject.

In preparing this edition we are much indebted to Professor R. E. Peierls, F.R.S., for providing us with a copy of his joint paper with Professors N. Bohr and G. Placzek in advance of publication and for reading certain parts of the manuscript, to Dr. E. H. S. Burhop for providing criticism of much of the manuscript and for great assistance in checking the proofs, to Dr. R. A. Buckingham for contributing to

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N. F. M.

H. S. W. M.

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January 1949

PREFACE TO FIRST EDITION

OUR aim in this book has been to give as complete an account as possible of the application of classical and quantum mechanics to collisions between atoms, electrons, and ions. We have paid special attention to collisions between particles moving with relatively small velocities, partly because most text-books treat only the scattering of fast particles, and partly because we hope that the theory will soon be applied to problems of chemical kinetics. We have not dealt with phenomena where one of the colliding particles is a light quantum, or with problems involving a discussion of nuclear structure.

We would like to express our thanks to Dr. C. B. O. Mohr, who has helped us in the preparation of the figures, and who has read much of the book in manuscript, and to Dr. Weisskopf, for assistance in proof-reading.

N. F. M.

H. S. W. M.

CAMBRIDGE

September 1933

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INTRODUCTION

MANY of the most important advances in physics have been due to the study of the behaviour of beams of charged particles. The researches of J. J. Thomson and others on cathode rays were responsible for the discovery of the electron and the measurement of the ratio of its charge to its mass. Similar methods enabled Kaufmann to demonstrate the relativistic variation of mass with velocity, and in the last decade the development of the method in the hands of Aston has led to our present knowledge of mass defects.

These experiments have yielded information about the nature of the charged particles themselves. Once their nature was understood, beams of charged particles have provided a most useful tool for the investigation of atomic structure. The most precise information can be obtained by bombarding matter, usually in the form of gas or a thin foil, under conditions such that very few of the incident particles make an effective collision with more than one atom. The conditions are then said to be such as to give 'single scattering'. One may then examine the energy and angular distribution of the scattered particles, or the radiation emitted by the atom.

The earliest experiment of this type was that of Rutherford, who bombarded a thin metal foil with a beam of α -particles. From the relation between the number of scattered particles and the thickness of the foil, he was able to show that the conditions were such as to give single scattering, and hence, from the variation of scattering with angle, he was led to postulate the heavy nucleus in the centre of the atom. Later developments have led to the discovery of anomalous scattering and of artificial disintegration, and have provided one of the most valuable methods of investigation of the nucleus.

Experiments in which atoms are bombarded by electrons of known energy have, in the hands of Franck, Hertz, and other workers, provided the most direct proof of the existence of the stationary states postulated by Bohr in 1913. It has been possible to measure the minimum energy required to excite the atom to a state from which it can radiate, and also to investigate the velocity distribution of the electrons after collision, and to show that scattered electrons have either lost no energy, or have lost more than the first resonance potential.

In these experiments the interest is concentrated more on the atom than on the colliding particle. It is the atom which has a planetary

structure, exists in stationary states, and radiates quanta of energy. Assuming the truth of these facts, the colliding particle behaves very much as one might expect, and provides a valuable tool for their investigation. Theoretical work has therefore, until very recently, been chiefly concerned with the stationary atomic states. This is also due to the accuracy and extent of the information about the energies of these states provided by spectroscopic methods. Early attempts were, however, made to obtain theoretical expressions for the *probability* that a colliding particle should lose energy. Thus in 1911 Bohr gave a semi-classical theory of the loss of energy of electrons and α -particles in passing through matter, from which he obtained an expression for the stopping-power which was qualitatively in agreement with experiment. Kramers in 1923 gave a theory of the emission of radiation by a particle on impact with a solid target. These formulae, while very useful as a basis with which to compare experimental results, admittedly did not rest on any secure theoretical basis.

It is one of the triumphs of the New Quantum Theory that it is able to answer questions of probability and intensity in collision problems in an unambiguous way. The first hint that classical mechanics, supplemented by quantum conditions, was inadequate in this field came from the work of Ramsauer and others, who showed that the cross-section of certain atoms in collisions with slow electrons was many times less than the gas-kinetic cross-section. But the great mass of experimental evidence is due to work carried out after the discovery of the new theory, and to some extent stimulated by it. Thus the work of Davisson and Germer and of G. P. Thomson and many others on the diffraction of electrons by crystals gives clear evidence of the wave nature of the electron. There is much experimental material concerned with the diffraction of electrons by gas atoms and molecules, most of which can be accounted for satisfactorily. There is also some evidence for the Pauli exclusion principle to be derived from collision phenomena.

The New Theory, besides accounting for these new and somewhat startling phenomena, is able to provide formulae for the stopping-power of various materials for α - and β -particles, the gas-kinetic cross-section of atoms, and many other quantities for which classical estimates have already been made. The formulae obtained from the Quantum Theory are usually in better agreement with the experiments than the older formulae, and such discrepancies as remain are probably due to the approximate mathematical methods which must be used to solve the equations, rather than to a defect in the theory itself (except in

the realm of high energy phenomena, where the theory is known to break down).

In this book, after an introductory chapter discussing the methods of the New Quantum Theory, we shall apply these methods to problems involving collisions between material particles, and show the agreement with experiment which has been obtained.

I

THE WAVE EQUATION

1. The wave function

IN this chapter we shall state the laws of wave mechanics, *not* in their most general form, applicable to any system however complicated, but in a simple way which can be applied only to the problem of the motion of a single charged particle in a field of force. The analysis of this chapter may also be applied to experiments in which the behaviour of a beam of electrons is investigated, provided that the interaction between the various electrons of the beam may be neglected, so that each electron behaves as though the other electrons were not there. In principle, this will of course be the case only if the charge density in the beam is vanishingly small.

We shall state the laws of wave mechanics with a view to their application to problems involving the motion of a free electron, and, since such experiments are usually carried out with beams of electrons, we shall first state the laws that describe the behaviour of steady beams.

These laws may be stated as follows: When we observe an electron, we observe a particle (a flash on a screen, a kick of a Geiger counter). If, however, we wish to know how many electrons there are likely to be in any volume, or how many cross unit area per unit time at a given point, we must assume the presence of a wave (the de Broglie wave). The amplitude and phase of this wave at a given point and given time is specified by a (complex) function of position† $\psi(x, y, z; t)$ (the wave function). This 'wave' makes its presence known to us through the following property: if $d\tau$ is an element of volume situated at the point (x, y, z) , then the probability that at the instant t an electron is in the volume-element $d\tau$ is

$$|\psi(x, y, z; t)|^2 d\tau.$$

The average number of electrons within a volume τ large enough to contain many electrons will then be

$$\int |\psi(x, y, z; t)|^2 d\tau,$$

the integration being throughout the volume τ . It is to be emphasized that the probabilities refer to the results of possible experiments; $|\psi|^2 d\tau$ gives the probability that an electron would be found in the volume $d\tau$, if an experiment were performed to look for it.

† (x, y, z) are Cartesian coordinates of position with respect to some axes fixed in space; t is the time coordinate.

In equation (18) we give a formula for the number of electrons crossing unit area per unit time.

We must now show how to calculate the wave function ψ that will describe correctly the behaviour of a beam of electrons in any given experiment; the method naturally depends on the kind of experiment that we have in mind. We may distinguish between two types: those in which we deal with a *steady* stream of electrons—e.g. the cathode rays in a highly evacuated discharge tube—and those in which we deal with a stream whose intensity varies with the time. The behaviour of a discharge tube when the current is first turned on presents a problem of the second type (cf. § 8).

2. Wave mechanics of steady beams of electrons

We shall first discuss the behaviour of steady streams of electrons. We shall limit ourselves in this chapter to the formulation of a non-relativistic theory, which will be valid only if the velocity of the electrons is small compared with that of light. The path of a beam of electrons is determined by the experimental conditions. If we wish to calculate the path of a beam of electrons, we must calculate ψ ; $|\psi|^2$ will then be equal to the number of electrons per unit volume at any point. Thus, given the experimental conditions, it must be possible to calculate $|\psi|$ at every point.

Suppose, for instance, that a beam of electrons of known energy is passed through a slit S into a highly evacuated enclosure, where the electrons describe a curved path due to an electric field. Then it must be possible, from the experimental conditions, to calculate the function $|\psi|^2$, and, if our rules for calculating $|\psi|^2$ are correct, we must find that $|\psi|^2$ vanishes outside the region where the electrons are observed, and is equal to the observed electron density inside it.

We must first know the wave-length of the waves under these conditions. On this point we have direct experimental evidence;† the observations on the diffraction of electrons by crystals show that, if electrons are accelerated by a known potential, the wave-length λ of the associated waves is given by the formula

$$\lambda = h/\sqrt{(2mW)}, \quad (1)$$

where W is the kinetic energy of each electron. The same formula was predicted by de Broglie in 1925 from theoretical considerations.‡

W here is a directly measurable quantity, $-W/\epsilon$ being the potential

† See, for instance, G. P. Thomson, *The Wave Mechanics of Free Electrons*, Chap. IV.

‡ See, for instance, Frenkel, *Wave Mechanics*, p. 19.

drop between the source of the electrons—where they may be considered approximately at rest—and the point where the wave-length is measured. In the experiment considered above, if W_0 is the kinetic energy of the electrons when they pass the slit S , then W at any other point is given by

$$W = W_0 - V(x, y, z),$$

where $V(x, y, z)$ is the potential energy of an electron at the point (x, y, z) , so that $V = -e\Phi(x, y, z)$, where Φ is the electrostatic potential difference between S and the point (x, y, z) . Thus the wave-length in an experiment of this type is given at every point of space. This argument is not valid if the fields are so strong that W changes appreciably in a distance comparable with a wave-length ($\sim 10^{-8}$ cm.). Such fields are only found within the atom.

The wave-length, in a given experiment, is thus known at every point. In order to calculate the wave function, we must know also the so-called 'boundary conditions'. These depend entirely upon the experiment under consideration; in the experiment referred to above, the 'boundary conditions' consist in a knowledge of the state of the wave over the surface of the slit—i.e. the wave amplitude, wave-length, and phase. These are clearly determined by the experimental conditions, except for the phase, which can be given any arbitrary value, since it does not affect $|\psi|$; moreover, it is clear from analogies with other kinds of wave motion that, given these conditions, the wave is determined at all points of space.

In order to calculate ψ we must know also the wave equation that it satisfies. Any monochromatic train of waves in a homogeneous isotropic medium must satisfy the equation

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0,$$

where λ is the wave-length. If the medium is not homogeneous, so that λ is a function of position, the amplitude of a wave train will satisfy the same equation *approximately*, provided that the variation in λ is small in a distance comparable with λ . Putting in the experimental value of λ , namely,

$$\lambda = h/\{2m(W_0 - V)\}^{\frac{1}{2}},$$

we have for the wave equation

$$\nabla^2\psi + \frac{8\pi^2m}{h^2}(W_0 - V)\psi = 0, \quad (2)$$

which is the wave equation of Schrödinger.

The condition given above, that λ shall not vary much in a distance comparable with λ itself, becomes, expressed in terms of V ,

$$|\text{grad } V|\lambda \ll W. \quad (3)$$

This will clearly be satisfied for all macroscopic fields. Subject to (3), we can show that the behaviour of a beam of electrons as predicted from Schrödinger's equation is the same as that predicted by Newtonian mechanics, as follows:

If a beam of waves moves in a medium of *varying* refractive index μ , the path of the beam is curved; the radius of curvature R at any point is given by the well-known formula

$$\frac{1}{R} = -\frac{\partial}{\partial n} \log \mu.$$

Now μ is the ratio of the wave-length at the point considered to the wave-length in free space; so that in our case

$$\mu = [W_0/(W_0 - V)]^\dagger,$$

and therefore

$$\frac{1}{R} = -\frac{\partial V}{\partial n} / 2(W_0 - V). \quad (4)$$

But, according to Newtonian mechanics, the beam will be bent in such a way that mv multiplied by the acceleration v^2/R normal to path of the electrons will be equal to the component $-\partial V/\partial n$ of the external force in this direction. Substituting

$$mv^2 = 2(W_0 - V)$$

we obtain (4). Thus the two systems of mechanics give the same results in this case.

We see therefore that wave mechanics will only give different results from classical mechanics when it is used to describe the behaviour of electrons in the strong fields that exist inside an atom. Before we can apply Schrödinger's equation (2) to such problems, there are two points that we must consider. Firstly, the quantity $V(x, y, z)$, the potential energy of an electron at the point (x, y, z) , is no longer a quantity which can be determined experimentally. According to the uncertainty principle, if the electron is observed to be at the point (x, y, z) , its velocity is unknown; and hence the change $V(x, y, z)$ in the kinetic energy as the electron travels from field-free space to (x, y, z) is not an observable quantity. Thus the only meaning that we can give to V is that it is a function which, when inserted in Schrödinger's equation, gives results in agreement with experiment. Of course, when we wish to calculate the behaviour of an electron in the field of a nucleus of charge E , our

first thought will be to use the Coulomb form of the potential

$$V(x, y, z) = -E\epsilon/r,$$

because this is the form of the potential energy of one macroscopic charged body in the field of another; but this procedure is only justified by the fact that it gives results in agreement with experiment; we have no *a priori* knowledge that this is the correct form, because $V(r)$ is not an experimentally measurable quantity.

The second point concerns the equation (2), and whether, whatever the form of V , it is the correct equation to use for atomic fields. We have seen that the equation (2), together with the probability interpretation of ψ (provided that they are applied to the behaviour of electrons in slowly varying fields), are *deductions* from the experiments on the diffraction of electrons by crystals. It is a new assumption that this equation may be applied to atomic fields. This assumption is only justified, naturally, if it gives results in agreement with experiment. The simplest test to which we can put the theory is to see whether it predicts the conservation of charge—i.e. whether it predicts that the average number of electrons going into any closed volume is equal to the number coming out of it. We shall see that this is so (§ 7).

Schrödinger's wave equation is therefore adopted because it is the simplest wave equation which gives:

- (1) the de Broglie wave-length for slowly varying fields;
- (2) the conservation of charge for all fields.

3. Examples of wave functions describing steady beams of electrons. Infinite plane wave

A beam of electrons of infinite breadth travelling from left to right along the z -axis is represented by the wave function†

$$\psi = A \exp 2\pi i(z/\lambda - \nu t), \quad (5)$$

where λ is the wave-length, given by

$$\lambda = h/\sqrt{(2Wm)}$$

(W = kinetic energy), and ν is the frequency, given by (cf. § 8)

$$\nu = W/h.$$

The number of electrons per unit volume is AA^* , and the number per unit time crossing unit area perpendicular to the z -axis is $AA^*\nu$, where ν is given by $\frac{1}{2}mv^2 = W$.

† It is often convenient to drop the time factor and to write only $A \exp(2\pi iz/\lambda)$.

4. Beam of electrons in field-free space

We suppose that the beam is formed by passing the electrons through a circular hole, of radius a , in a screen. Let us choose axes with the origin at the centre of the hole, and the axes of x and y in the plane of the screen. The direction of motion of the electrons will then be along the axis. We have to form our wave function by superimposing plane waves of wave-length λ , all travelling in directions very nearly parallel to the z -axis, in such a way that, in the xy -plane, ψ will vanish

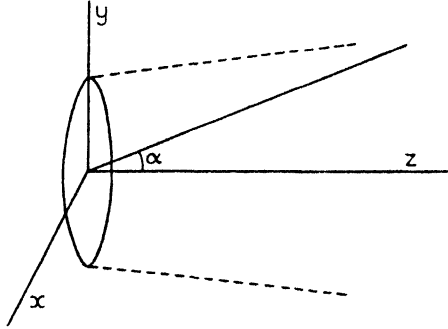


FIG. 1

outside the circular hole. Now the equation of a plane wave travelling in the direction given by the polar angles† α , β is

$$A \exp \left[\frac{2\pi i}{\lambda} (z \cos \alpha + x \sin \alpha \cos \beta + y \sin \alpha \sin \beta) \right].$$

It follows that our wave function ψ must be of the form

$$\psi = \iint A(\alpha, \beta) \exp \left[\frac{2\pi i}{\lambda} (z \cos \alpha + x \sin \alpha \cos \beta + y \sin \alpha \sin \beta) \right] d\alpha d\beta, \quad (6)$$

where $A(\alpha, \beta)$ must be chosen in such a way that ψ vanishes in the xy -plane, outside the circular aperture. If we transform to spherical polar coordinates (r, θ, ϕ) (6) becomes

$$\psi = \iint A(\alpha, \beta) \exp \left[\frac{2\pi i}{\lambda} r \{ \cos \theta \cos \alpha + \sin \theta \sin \alpha \cos(\phi - \beta) \} \right] d\alpha d\beta.$$

It is clear from the symmetry of the problem that A is a function of α only; carrying out the β integration we obtain

$$\psi = 2\pi \int_0^{\pi} A(\alpha) d\alpha \exp \left(\frac{2\pi i r}{\lambda} \cos \theta \cos \alpha \right) J_0 \left(\frac{2\pi r}{\lambda} \sin \theta \sin \alpha \right). \quad (7)$$

† i.e. if l, m, n are the direction cosines,

$$l = \sin \alpha \cos \beta, \quad m = \sin \alpha \sin \beta, \quad n = \cos \alpha.$$

To find $A(\alpha)$ we use the fact that ψ is given equal to some function $f(r)$, say, on the xy -plane, i.e. on the plane $\theta = \frac{1}{2}\pi$; we have then

$$f(r) = 2\pi \int_0^{\frac{1}{2}\pi} A(\alpha) d\alpha J_0\left(\frac{2\pi r}{\lambda} \sin \alpha\right). \quad (8)$$

From this integral equation $A(\alpha)$ must be determined.

The simplest convenient expression for $f(r)$ is

$$f(r) = B \exp(-r^2/a^2). \quad (9)$$

In practice $f(r)$ would be more complicated than this, being constant within the hole ($r < a$), and falling to zero in some irregular way at the boundary. We adopt the simplified form (9) because it makes possible the exact solution of (8). If we put

$$A(\alpha) = C e^{-(\sin \alpha/\sigma)^2} \sin \alpha \cos \alpha$$

with

$$\sigma = \lambda/\pi a, \quad C\pi\sigma^2 = B,$$

then equation (8) is satisfied† if we replace the upper limit of integration by ∞ , a step which may easily be justified since $\sigma \ll 1$.

We have now to integrate (7). Since the whole value of the integral comes from small α , we replace (7) by

$$\psi = 2\pi C \int_0^{\infty} e^{-\alpha^2/\sigma^2} \exp\left[\frac{2\pi i r \cos \theta}{\lambda} (1 - \frac{1}{2}\alpha^2)\right] J_0\left(\frac{2\pi r \alpha}{\lambda} \sin \theta\right) \alpha d\alpha,$$

which is equal to

$$\pi C \left\{ \frac{1}{\sigma^2} + \frac{\pi i r \cos \theta}{\lambda} \right\}^{-1} \exp\left[-\frac{\pi^2 r^2}{\lambda^2} \sin^2 \theta \left\{ \frac{1}{\sigma^2} + \frac{\pi i r \cos \theta}{\lambda} \right\}^{-1} \right] \exp\left(\frac{2\pi i z}{\lambda}\right), \quad (10)$$

which is the required wave function. The number of particles per unit volume is $|\psi|^2$, which, for large r , tends to

$$(C\lambda/r)^2 \exp(-2 \sin^2 \theta/\sigma^2),$$

which is equal to

$$|\psi|^2 \sim (\pi B a^2/\lambda r)^2 \exp(-2\pi^2 a^2 \sin^2 \theta/\lambda^2). \quad (11)$$

The diffraction of the beam is well shown.

5. One-dimensional problems

Let us suppose that a beam of electrons, such as the beam discussed in the last section, moving along the z -axis, enters a field which varies only

† Cf. Watson, *Theory of Bessel Functions*, p. 393. We use the formula

$$\int_0^{\infty} J_0(at) e^{-t^2/\sigma^2} t dt = \frac{1}{2} \sigma^2 e^{-\frac{1}{2}a^2\sigma^2}.$$

in the z -direction, so that the potential energy of an electron in this field is of the form $V(z)$. It is required to calculate the behaviour of the beam.

In such problems the variation of ψ with x, y is not relevant; for purposes of calculation it is therefore convenient to take the incident beam of infinite extent, so that it may be represented by an infinite plane wave. The complete wave function ψ will then be a function of z only, and will therefore satisfy the wave equation

$$\frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2}(W - V)\psi = 0, \quad (12)$$

where W is the kinetic energy of each electron at the point where V is considered zero.

As an example† we shall investigate the behaviour of a beam of electrons impinging on a potential jump, that is to say, a field such that

$$\begin{aligned} V &= 0 & (z < 0), \\ V &= U & (z > 0). \end{aligned}$$

We shall suppose that $U < W$. We represent the incident wave, falling on the potential jump, by

$$A \exp(ikz) \quad (z < 0),$$

where

$$k = 2\pi mv/h = 2\pi(2mW)^{1/2}/h.$$

This represents a beam of electrons moving with velocity v , and such that AA^*v cross unit area per unit time. For the reflected beam we take

$$B \exp(-ikz) \quad (z < 0),$$

and for the transmitted beam

$$C \exp(ik'z) \quad (z > 0),$$

where

$$k' = 2\pi mv'/h = 2\pi[2m(W - U)]^{1/2}/h.$$

Thus for our complete wave function we have

$$\begin{aligned} \psi &= A \exp(ikz) + B \exp(-ikz) & (z < 0), \\ \psi &= C \exp(ik'z) & (z > 0). \end{aligned}$$

We now put in the boundary conditions satisfied by the wave function at $z = 0$. These are that ψ and $d\psi/dz$ must be continuous. We have therefore

$$\begin{aligned} A + B &= C, \\ k(A - B) &= Ck'. \end{aligned}$$

† A discussion of the passage of electrons across potential barriers is given in various text-books. Cf. Mott and Sneddon, *Wave Mechanics and its Application*, Chap. I; Frenkel, *Wave Mechanics*, § 15; Condon and Morse, *Quantum Mechanics*, pp. 222 et seq.; also in Condon, *Rev. Mod. Phys.* 3 (1931), 43. A summary of the application of these ideas to electron emission from metals is given by Nordheim, *Phys. Zeits.* 30 (1929), 177.

Solving, we obtain

$$B = A(k-k')/(k+k'),$$

$$C = 2Ak/(k+k').$$

The number of particles crossing unit area per unit time in the reflected beam is

$$AA*v(k-k')^2/(k+k')^2,$$

and in the transmitted beam

$$AA*v'(2k)^2/(k+k')^2.$$

Remembering that $k/k' = v/v'$, we see that the fraction of the total number of particles reflected is

$$(v-v')^2/(v+v')^2$$

and the fraction transmitted

$$4vv'/(v+v')^2.$$

We see that the two proportions add up to unity, so that the wave function predicts that electrons are conserved. This is a particular case of a general law proved below in § 7.

6. Solution of the wave equation for an electron in a slowly varying field†

If the potential energy $V(z)$ does not vary appreciably in a distance comparable with the wave-length $h/\sqrt{\{2m(W-V)\}}$, one may obtain an approximate solution of the wave equation as follows. We write

$$\frac{8\pi^2m}{h^2}(W-V) = f(z),$$

and assume $f(z)$ positive in the range of z considered. Schrödinger's equation becomes

$$\frac{d^2\psi}{dz^2} + f(z)\psi = 0. \quad (13)$$

We write

$$\psi = Ae^{i\beta}; \quad (14)$$

substituting into (13) we obtain

$$A'' + 2iA'\beta' + i\beta''A - \beta'^2A + fA = 0, \quad (15)$$

where the dashes denote differentiation with respect to z . We put

$$\beta'^2 = f(z),$$

which gives

$$\beta = \int [f(z)]^{\frac{1}{2}} dz.$$

Since f is nearly a constant in a range of z long compared with the wave-length, this gives for β in such a range,

$$\beta \simeq f^{\frac{1}{2}}z + \text{const.}$$

† This method is due to Jeffreys, *Proc. Lond. Math. Soc.* Ser. 2, 23, Part 6.

It follows from (14) that A to a first approximation is constant in such a range, and hence that

$$A'' \ll A'f^{\frac{1}{2}} \ll Af.$$

Hence in (15) we may neglect A'' in comparison with $A'\beta'$ [we cannot neglect $A'\beta'$ in comparison with $A\beta''$ because β'' is itself small]. We thus obtain from (15)

$$2A'\beta' + \beta''A = 0,$$

and hence

$$A = \text{const.} [f(z)]^{-\frac{1}{2}}.$$

Thus our approximate solution is

$$\psi = [f(z)]^{-\frac{1}{2}} \exp\left\{\pm i \int^z [f(z)]^{\frac{1}{2}} dz\right\}. \quad (16)$$

The number N of electrons crossing unit area per unit time is equal to $|\psi|^2$ multiplied by the velocity of the electrons. Now

$$|\psi|^2 = [f(z)]^{-1}$$

and the velocity of the electrons is $[2(W-V)/m]^{\frac{1}{2}}$, which is proportional to $[f(z)]^{\frac{1}{2}}$. Thus N is the same for all z , as it should be.

Similarly, it may be shown that, if $f(z)$ is negative, then, if we write

$$g(z) = -f(z) = \frac{8\pi^2 m}{h^2} (V - W),$$

the approximate solutions of the wave equation (13) are

$$[g(z)]^{-\frac{1}{2}} \exp\left\{\mp \int^z [g(z)]^{\frac{1}{2}} dz\right\}.$$

In many problems $f(z)$ has a zero z_0 such that

$$f(z) > 0 \quad (z > z_0)$$

$$f(z) < 0 \quad (z < z_0),$$

and we require to know the particular solution which *decreases* as z becomes less than z_0 . It has been shown by Jeffreys† that, if $f'(z_0) \neq 0$, then in the range $z > z_0$ this solution is

$$\psi = f^{-\frac{1}{2}} \sin\left[\frac{1}{4}\pi + \int_{z_0}^z [f(z)]^{\frac{1}{2}} dz\right]. \quad (17)$$

7. Formulae for the current; the conservation of charge

We have postulated as an axiom that the quantity $\psi\psi^*$ shall be equal to the number of electrons per unit volume in the beam of electrons described by the wave function ψ , or more exactly, that $\psi\psi^* d\tau$ is equal

† Loc. cit.

to the probability that an electron will be found in the volume-element $d\tau$. We can obtain a similar formula for the current, or number of electrons crossing a given area per unit time. More exactly, we require a vector \mathbf{j} , at all points of space, such that $(\mathbf{j} \cdot d\mathbf{S}) dt$ is the probability that an electron will cross an element $d\mathbf{S}$ of area in the time dt . The required formula for \mathbf{j} is

$$\mathbf{j} = \frac{\hbar}{4\pi im} \{\psi^* \text{grad } \psi - \psi \text{grad } \psi^*\}. \quad (18)$$

We shall show that this formula gives \mathbf{j} correctly in all cases in which \mathbf{j} could be measured.

In a region in which V is constant or zero, and in which there is a single stream of electrons moving in the direction \mathbf{n} , the wave function will be of the form

$$\psi = a \exp\{2\pi imv \mathbf{n} \cdot \mathbf{r}/\hbar\}$$

and \mathbf{j} equal to $v|a|^2 \mathbf{n}$, which is clearly given by (18).

To measure \mathbf{j} in general, one would place a collector in the path of the electrons, and measure the charge falling on it per unit time. Such a procedure measures the average value of \mathbf{j} over a region large compared with the wave-length, and this is the only thing that can be determined by direct experiment. If we suppose that V and therefore λ are constant in this region, then the wave function must be of the form

$$\psi = \sum_s a_s \exp\{2\pi imv \mathbf{n}_s \cdot \mathbf{r}/\hbar\},$$

where the \mathbf{n}_s are unit vectors, and the a_s constants. This wave function represents streams of electrons superimposed on one another. The fact that according to the wave mechanics such streams should interfere will not affect the number of electrons falling on the collector, because the collector is large compared to the wave-length. If the area of the collector is A , and if it is normal to the direction \mathbf{n} , the number of electrons falling on it per unit time is

$$vA \sum_s |a_s|^2 \mathbf{n} \cdot \mathbf{n}_s. \quad (19)$$

According to the formula (18) this number should be

$$\int \mathbf{j} \cdot \mathbf{n} dS$$

over the surface of A . This is easily seen to lead to the formula (19), since the cross terms of the type

$$a_s a_t^* \exp\{2\pi imv (\mathbf{n}_s - \mathbf{n}_t) \cdot \mathbf{r}/\hbar\}$$

become zero when averaged over an area large compared with the wave-length.

If the beams come from different sources, α_s must be taken to have the form $\alpha_s \exp(i\phi_s)$, where ϕ_s is an arbitrary phase having no relation to the corresponding phase ϕ_t . To obtain the current one must average (18) for all ϕ_s, ϕ_t ; the cross terms will then vanish.

We shall refer to the vector \mathbf{j} as the current vector, though it is only the averaged value of \mathbf{j} that can be observed directly.

It may easily be shown from the wave equation that charge is conserved—i.e. that the average number of electrons moving into a volume is, in a steady beam, equal to the number moving out.† This will be so if $\text{div } \mathbf{j}$ vanishes. Now from (18) we have

$$\text{div } \mathbf{j} = \frac{\hbar}{4\pi im} \{\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*\}.$$

But since both ψ and ψ^* satisfy Schrödinger's equation, it follows that

$$\psi^* \nabla^2 \psi = -\psi^* \frac{8\pi^2 m}{\hbar^2} (W - V) \psi$$

and that $\psi \nabla^2 \psi^*$ is equal to the same expression. Thus we see that $\text{div } \mathbf{j}$ is zero.

It is of interest to note that the absorption of particles from a beam may be represented by the introduction of a negative imaginary potential energy in the Schrödinger equation. If the particles are absorbed at a rate $\alpha\rho$ per unit volume per second where ρ is the density, then, in a steady state,

$$\text{div } \mathbf{j} + \alpha\rho = 0. \quad (19a)$$

Writing, in (12),

$$V = V_r - iV_i,$$

where V_r, V_i are real functions of r , then

$$\psi^* \nabla^2 \psi = -\psi^* \frac{8\pi^2 m}{\hbar^2} (W - V_r + iV_i) \psi,$$

$$\psi \nabla^2 \psi^* = -\psi^* \frac{8\pi^2 m}{\hbar^2} (W - V_r - iV_i) \psi^*,$$

$$\text{so} \quad \text{div } \mathbf{j} = \frac{\hbar}{4\pi mi} (\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*) = -4\pi V_i \psi \psi^* / \hbar.$$

Comparing with (19a) we have $\alpha = 4\pi V_i / \hbar$.

Use will be made of this result in Chap. VIII, § 8.31.

8. Problems in which $|\psi|^2$ varies with the time

Let us consider a highly evacuated discharge tube, in which a beam of electrons is projected against a screen in which there is an aperture covered by a shutter. Suppose that the aperture is suddenly opened; then, a short time t afterwards, there would be a stream of electrons coming out of the aperture, and extending a distance vt from the hole.

† Compare Sommerfeld, *Wave Mechanics*, p. 89.

v is what we call the 'velocity' of the electrons, and is connected with the energy W due to the field that has accelerated them by the formula

$$W = \frac{1}{2}mv^2.$$

From the point of view of the classical mechanics this is trivial; however, according to our fundamental assumption, we ought to be able to predict this result by postulating the presence of a wave and then making the assumption that $|\psi|^2$ is equal to the number of electrons per unit volume. Now, from the wave point of view, we have a steady wave train falling on the screen, until the shutter is opened, when a beam passes out into space; the velocity with which the front of the beam advances is the *group velocity* of the waves.

Now the group velocity in any wave-motion is equal to $d\nu/dN$, where ν is the frequency, and N the wave number, equal to the reciprocal of the wave-length λ . In order that the wave description may be in agreement with experiment (that is, in this case, with the classical theory), this velocity must be equal to the classical velocity of the electrons, namely, v . Thus we must have

$$\frac{d\nu}{dN} = v.$$

Expressing v in terms of N , we have

$$\frac{d\nu}{dN} = hN/m.$$

We may integrate this equation; we obtain

$$\begin{aligned} \nu &= \frac{1}{2}hN^2/m + \text{const.} \\ &= W/h + \text{const.} \end{aligned}$$

The formula

$$h\nu = E,$$

where E is the relativistic expression for the energy of a particle (including the rest-mass), namely,

$$E = mc^2(1 - v^2/c^2)^{-\frac{1}{2}},$$

was deduced by de Broglie† from considerations depending on the principle of relativity. If v/c is small compared with unity, this reduces to

$$h\nu = mc^2 + \frac{1}{2}mv^2,$$

which gives a value to the constant. However, the value of this constant does not affect any experimental result, and it is convenient to put it equal to zero in non-relativistic problems.

† de Broglie, *Ann. de Physique*, 10 (1925), 22.

The wave equation for a general, non-monochromatic wave disturbance is

$$\frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t} = \frac{\hbar^2}{8\pi^2 m} \nabla^2 \psi - V\psi. \quad (20)$$

This equation may most easily be obtained as follows: the equation satisfied by the wave function describing a stream of electrons of energy W is

$$\nabla^2 \psi + \frac{8\pi^2 m}{\hbar^2} (W - V)\psi = 0. \quad (21)$$

This wave function will be of the form

$$\psi = f(x, y, z) \exp(-2\pi i Wt/\hbar), \quad (22)$$

as we have just shown. Now the equation which we require must not contain W ; from (22) we see that

$$W\psi = -\frac{\hbar}{2\pi i} \frac{\partial \psi}{\partial t},$$

and hence, from (21), it follows that equation (20) is satisfied by wave functions describing electrons all with the same energy—i.e. by wave functions of the type (22). But the most general wave function must be made up by superimposing such wave functions; therefore the most general wave function will satisfy (20).

From the wave equation (20) it may easily be shown that charge is conserved. If we denote by ρ the quantity $\psi\psi^*$, then $\int \rho d\tau$ integrated over any volume will be equal to the probability that an electron is in the volume. $\int \mathbf{j} \cdot d\mathbf{S}$ will be equal to the probability per unit time that an electron moves out of the volume. We must therefore have

$$\frac{\partial}{\partial t} \int \rho d\tau + \int \mathbf{j} \cdot d\mathbf{S} = 0. \quad (23)$$

This will be the case if $\frac{\partial \rho}{\partial t} + \text{div } \mathbf{j} = 0$. (24)

(24) may easily be proved from the wave equation (20), using the definition (18) of \mathbf{j} . For proof cf. Sommerfeld, *Wave Mechanics*, p. 89.

9. Wave packets

Let us suppose that a beam of electrons is fired at a screen in which there is an aperture, which is initially closed by some kind of shutter, and is then opened for a short time, and then closed again. If this experiment were carried out, a cloud of electrons would pass through the aperture and travel out into space. One could say that a region, in which the electron density is different from zero, would be travelling

through space. The shorter the time during which the shutter is open, the smaller will this region be.

To describe this phenomenon in the language of wave mechanics, we must picture a train of de Broglie waves falling on the screen, and, when the shutter is opened, a 'wave packet' or 'wave group' passing through. The square of the amplitude of the wave function gives us, as usual, the probable electron density. The wave group as a whole will travel forward with the group velocity of the de Broglie waves, and this, as we have seen, is equal to the classical velocity of the electrons that they represent. The wave mechanics, therefore, makes the same predictions as the classical mechanics.

If $\psi(x, y, z, t)$ is the wave function at any point in the wave packet, then the number n , defined† by the integral (over all space)

$$n = \iiint |\psi(x, y, z, t)|^2 dx dy dz,$$

is equal to the probable number of electrons that have passed through the shutter. If the original electron beam were sufficiently weak, or if the shutter were only open for a very short time, then this number might be of order of magnitude unity. It must be remembered, of course, that if n were actually equal to unity, it would not mean that just one electron would pass through every time. It would mean that, if the experiment were repeated a very large number p times, the total number of electrons passing through would be pn , even though in individual experiments the number would be zero, one, two, and so on.

In discussing the behaviour of wave packets, it is usual to normalize the wave function in such a way that n is equal to unity.

The study of wave packets is of little use in enabling one to predict the results of real experiments; in practically all experiments with free electrons a continuous stream is used. Wave packets are, however, instructive in enabling one to understand the ideas of the wave mechanics, because they have a certain rather superficial resemblance to the *particles* of the classical theory. For instance, if one can show that a wave packet will follow the path of the classical particle, one may deduce that wave mechanics and classical mechanics will give the same result in a given problem.

9.1. *One-dimensional motion of a wave packet in a homogeneous medium*

In any kind of wave-motion there is a relation between the frequency ν and the wave number N . For de Broglie waves, in the non-relativistic theory, this relation is

$$\nu = \frac{1}{2}hN^2/m.$$

† n is a constant with respect to the time; cf. § 8.

We shall assume in this paragraph a quite general relationship,

$$\nu = \nu(N).$$

The most general possible wave disturbance is given by

$$\psi = \int_{-\infty}^{+\infty} a(N) dN \exp[2\pi i(Nz - \nu t)],$$

where $a(N)$ is an arbitrary complex function. This wave disturbance is obtained by superimposing an infinite number of plane waves, with arbitrary amplitudes and phases. We can choose $a(N)$ so that ψ has any desired form at time $t = 0$, by means of Fourier's integral theorem. We shall take for our wave packet at time $t = 0$

$$\psi = C \exp(2\pi i N_0 z - z^2/\sigma^2). \quad (25)$$

The error function form for the amplitude is chosen because all the subsequent integrations can then be carried out in terms of known functions. The wave packet is thus initially in the neighbourhood of the origin, has wave-number N_0 , and breadth of order of magnitude 2σ . It is easily seen (and will be proved below) that

$$a(N) = C\pi^{\frac{1}{2}}\sigma \exp[-(N - N_0)^2\pi^2\sigma^2]. \quad (26)$$

To find the form of the wave packet at any subsequent time, we have therefore to evaluate the integral

$$\psi = \int_{-\infty}^{\infty} C\pi^{\frac{1}{2}}\sigma \exp[2\pi i(Nz - \nu t) - (N - N_0)^2\pi^2\sigma^2] dN. \quad (27)$$

To do this we expand ν in a Taylor's series

$$\nu = \nu_0 + (N - N_0)\nu'_0 + \frac{1}{2}(N - N_0)^2\nu''_0 + \dots,$$

where ν_0, ν'_0 , etc., denote the values of ν and its differential coefficients with respect to N , for the value $N = N_0$. Now if $\sigma \gg \lambda$, as we may assume to be the case, it is clear that most of the integral (27) comes from $N \sim N_0$; we shall therefore secure a good approximation if we neglect terms in $(N - N_0)^3$ in the expansion of ν . We may note that for de Broglie waves in the non-relativistic theory this approximation is exact, since ν is a quadratic function of N .

Writing $N - N_0 = \zeta$,
the equation (27) becomes

$$\psi = C\pi^{\frac{1}{2}}\sigma \int_{-\infty}^{+\infty} \exp[-a\zeta^2 + 2b\zeta + c] d\zeta,$$

where

$$\begin{aligned} a &= \pi^2 \sigma^2 + \pi i \nu_0'' t, \\ b &= -\pi i (\nu_0' t - z), \\ c &= 2\pi i (N_0 z - \nu_0 t). \end{aligned}$$

The integrand may be written

$$\exp\left[-a\left(\zeta - \frac{b}{a}\right)^2 + c + \frac{b^2}{a}\right].$$

Putting $\zeta - b/a = \eta$, we obtain for ψ

$$\begin{aligned} \psi &= C\pi^{\frac{1}{2}}\sigma \exp\left(c + \frac{b^2}{a}\right) \int_{-\infty}^{\infty} e^{-a\eta^2} d\eta, \\ &= C\pi\sigma a^{-\frac{1}{2}} \exp\left(c + \frac{b^2}{a}\right). \end{aligned}$$

Putting in the values of a , b , c , we obtain

$$\psi = C\left[1 + \frac{i\nu_0'' t}{\pi\sigma^2}\right]^{-\frac{1}{2}} \exp\left[2\pi i(N_0 z - \nu_0 t) - \frac{(\nu_0' t - z)^2}{\sigma^2 + i\nu_0'' t/\pi}\right].$$

The wave packet reduces to (25) at time $t = 0$, as it should. At time t the centre of the wave packet is at the point

$$z = \nu_0' t.$$

Thus the velocity of the wave packet is equal to the group velocity $d\nu/dN$. A further important property of the wave packet is the spreading. Considering the exponential term in ψ only, we have for the amplitude $|\psi|$,

$$\exp\left[\frac{-\sigma^2(\nu_0' t - z)^2}{\sigma^4 + (\nu_0'' t/\pi)^2}\right].$$

For large t , therefore, the breadth of the wave packet is of order of magnitude

$$2\nu_0'' t/\pi\sigma.$$

The wave packet therefore spreads as it goes along, and the velocity with which its length increases is

$$\frac{d^2\nu}{dN^2} \frac{2}{\pi\sigma}.$$

If the waves are de Broglie waves,† we have in the non-relativistic theory

$$\frac{d\nu}{dN} = \frac{hN}{m} = v \quad \text{and} \quad \frac{d^2\nu}{dN^2} = \frac{h}{m}.$$

† Wave packets of de Broglie waves have been considered by various authors. Darwin (*Proc. Roy. Soc. A* 117 (1927), 258) has given the wave function for a three-dimensional wave packet in free space (eq. (5.6)), a wave packet describing an electron under a constant electric force (eq. (6.2)), and under constant magnetic field (eq. (7.10)). Wave packets are discussed by Condon and Morse, *Quantum Mechanics*, p. 219; Frenkel, *Wave Mechanics*, p. 60.

We have therefore for ψ

$$\psi = C \left[1 + \frac{i\hbar t}{\pi m \sigma^2} \right]^{-\frac{1}{2}} \exp \left[\frac{-(vt-z)^2}{\sigma^2 + i\hbar t/\pi m} - 2\pi i \left(\frac{mv^2 t}{2\hbar} - \frac{mvz}{\hbar} \right) \right].$$

One of the most important properties of wave packets is that, if a wave packet passes through any electric or magnetic field which does not vary appreciably in a distance comparable with the size of the wave packet, then it will follow the classical path. A proof is given in various text-books.†

† See, for example: Dirac, *Quantum Mechanics*, 3rd edition, p. 121; Fronkel, *Wave Mechanics, Elementary Theory*, 2nd edition, § 9; Debye, *Phys. Zeitschrift*, **28** (1927), 170; Ehrenfest, *Zeits. f. Physik*, **45** (1927), 455; Ruark, *Phys. Rev.* **32** (1928), 1133; Mott and Sneddon, *Wave Mechanics and its Applications*, p. 28.

II

THE THEORY OF THE SCATTERING OF A BEAM OF PARTICLES BY A CENTRE OF FORCE

1. Calculation of scattered intensity

THE problem of the collision between an electron and an atom is a 'many-body' problem, and as such will be considered in Chapter VIII; in this chapter we shall consider the scattering of a stream of charged particles by a small spherically symmetrical region in which their potential energy is different from zero; we shall call this region the 'atom', and the potential energy of a particle at distance r from the nucleus will be denoted by $V(r)$. In Chapter VIII it is shown that the elastic scattering by atoms can, to a certain approximation, be treated in this way, and methods are given for the calculation of $V(r)$.

In experiments on the scattering of a beam of particles, one measures the number of scattered particles falling per unit time on an area dS placed at a distance r from the scattering atoms. For purposes of calculation we suppose that there is only one scattering atom. The number of particles falling on dS will then be proportional to the area dS and inversely to the square of the distance r . That is to say, the number is proportional to the solid angle $d\omega$ subtended by dS at the centre of the atom. We shall refer to the particles which hit dS as 'scattered through an angle θ into the solid angle $d\omega$ '.

The number of particles scattered into the solid angle $d\omega$ is also proportional to the current per unit area in the incident beam. Suppose that N particles cross unit area per unit time in the incident beam. Let the number of particles scattered per unit time through an angle θ into the solid angle $d\omega$ be

$$NI(\theta) d\omega.$$

Then $I(\theta)$ is the quantity that we wish to calculate. $I(\theta) d\omega$ has the dimensions of an area, and will be referred to either as the effective cross-section for scattering into the solid angle $d\omega$ or as the differential cross-section.

We shall refer, in what follows, to the charged particles as electrons, though the analysis is applicable equally to any type of particle.

Let (x, y, z) denote the Cartesian coordinates of the electron at any moment, and (r, θ, ϕ) its spherical polar coordinates, the z -axis being the axis from which θ is measured.† We shall suppose the atom to be

† i.e. $r \cos \theta = z$, $r \sin \theta e^{i\phi} = x + iy$.

situated at the origin, and the potential energy of an electron distant r from the origin to be $V(r)$. In this section we shall assume that $V(r)$ tends to zero faster than $1/r$; the case of Coulomb scattering will be considered in Chapter III. We shall suppose that a stream of electrons moves with velocity v from left to right along the z -axis. We represent this stream of electrons by the plane wave $\exp(ikz)$, where k is equal to $2\pi mv/h$. This wave represents a density of electrons of one per unit volume, and therefore a flow of v electrons across unit area per unit time. The wave will be scattered by the atom, the amplitude of the scattered wave at the point (r, θ, ϕ) being, let us say,

$$r^{-1}f(\theta)e^{ikr}.$$

Our problem is to find the function $f(\theta)$. From it we can deduce the number scattered into a given solid angle per unit time. The number of electrons in the scattered wave crossing an element of area dS at the point (r, θ, ϕ) is $vr^{-2}dS|f(\theta)|^2$ per unit time; and therefore, if the incident beam is such that *one* electron falls on unit area per unit time, the number $I(\theta)d\omega$ scattered into a given solid angle $d\omega$ per unit time is equal to $|f(\theta)|^2d\omega$. We have therefore

$$I(\theta) = |f(\theta)|^2.$$

The number of particles scattered between angles θ and $\theta+d\theta$ is

$$|f(\theta)|^2 2\pi \sin \theta d\theta.$$

Our problem, then, is to find a solution ψ of the wave equation which, at a large distance from the atom, represents an incident wave and a scattered wave. That is to say, we must have, for large r ,

$$\psi \sim e^{iks} + r^{-1}e^{ikr}f(\theta). \quad (1)$$

The wave equation satisfied by ψ (Schrödinger's equation) may be written

$$\nabla^2\psi + [k^2 - U(r)]\psi = 0, \quad (2)$$

where $k = 2\pi mv/h$, $U(r) = \frac{8\pi^2m}{h^2}V(r)$.

Before considering the solution of (2) we require a certain expansion in spherical harmonics (eq. (8)), which will now be proved.

The plane wave e^{iks} is a solution of the equation

$$\nabla^2\psi + k^2\psi = 0. \quad (3)$$

The equation can also be solved in spherical polar coordinates; it is easily seen that

$$\psi = P_n(\cos \theta)f_n(r)$$

is a solution, if f_n is a solution of the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{df}{dr} \right) + \left(k^2 - \frac{n(n+1)}{r^2} \right) f = 0 \tag{4}$$

and $P_n(\cos \theta)$ is the n th Legendre coefficient.† The equation (4) can be solved in series; there are two solutions, one beginning with r^n and the other with r^{-n-1} ; they are expressible in terms of Bessel functions (cf. eq. (9)). Let us denote by $f_n(r)$ the solution of (4) that is bounded at $r = 0$. Then, except for an arbitrary multiplying constant, $f_n(r)$ is determined.

Clearly, if the A_n are arbitrary constants,

$$\sum_{n=0}^{\infty} A_n P_n(\cos \theta) f_n(r) \tag{5}$$

is a solution of (3), and we know further that this is the most general solution of (3) which has axial symmetry (i.e. does not involve ϕ), and which is finite at the origin. It follows that e^{ikz} can be expanded in this form.

Let, then,
$$e^{ikz} = e^{ikr \cos \theta} = \sum_{n=0}^{\infty} A_n P_n(\cos \theta) f_n(r).$$

To obtain A_n we multiply both sides by $P_n(\cos \theta) \sin \theta$ and integrate from 0 to π . Putting $\cos \theta = t$, we obtain

$$\frac{2}{2n+1} A_n f_n(r) = \int_{-1}^{+1} e^{ikrt} P_n(t) dt. \tag{6}$$

f_n has been defined except for an arbitrary multiplying constant, and A_n cannot be determined until this is given. We can define f_n exactly by means of its asymptotic expansion for large r ; integrating the right-hand side of (6) by parts, we obtain

$$\frac{1}{ikr} [e^{ikrt} P_n(t)]_{t=-1}^{t=+1} - \frac{1}{ikr} \int_{-1}^{+1} e^{ikrt} P_n'(t) dt.$$

The second term is of order $1/r^2$; for large r , therefore, we have

$$\frac{2}{2n+1} A_n f_n(r) \sim \frac{1}{ikr} [e^{ikrt} P_n(t)]_{-1}^{+1}.$$

Since $P_n(1) = 1$, $P_n(-1) = (-1)^n$, the right-hand side of this equation is equal to

$$2i^n (kr)^{-1} \sin(kr - \frac{1}{2}n\pi).$$

If now we determine f_n completely by stipulating that it shall be that

† Whittaker and Watson, *Modern Analysis*, p. 302.

solution of (4) which has the asymptotic form

$$f_n(r) \sim (kr)^{-1} \sin(kr - \frac{1}{2}n\pi), \quad (7)$$

then we see that A_n is equal to $(2n+1)i^n$, and therefore

$$e^{ikz} = \sum_{n=0}^{\infty} (2n+1)i^n P_n(\cos\theta) f_n(r), \quad (8)$$

which is the required expansion. For reference we give here the expressions for f_n in terms of Bessel functions, viz.

$$\begin{aligned} f_0(r) &= \sin kr/kr, \\ f_n(r) &= (\pi/2kr)^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr). \end{aligned} \quad (9)$$

Let us now consider the wave equation (2) for an electron in the field of an atom. As before, the general solution of (2) having axial symmetry is

$$\psi = \sum_{n=0}^{\infty} A_n P_n(\cos\theta) L_n(r), \quad (10)$$

where the A_n are arbitrary constants, and L_n is any solution of

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dL}{dr} \right) + \left(k^2 - U(r) - \frac{n(n+1)}{r^2} \right) L = 0. \quad (11)$$

As before, (11) has two independent solutions,† one finite at the origin and the other infinite. We wish to choose the constants A_n so that (10) shall represent an incident wave and a scattered wave—i.e. so that (10) shall have the asymptotic form (1). It is necessary that our wave function should be everywhere finite; L_n must therefore be chosen to be that solution of (11) that is finite at the origin. $L_n(r)$ is then defined except for an arbitrary multiplying constant.

If we set $L_n(r) = r^{-1}G(r)$, equation (11) reduces to

$$\frac{d^2G}{dr^2} + \left[k^2 - U(r) - \frac{n(n+1)}{r^2} \right] G = 0. \quad (12)$$

For large r the last two terms in the bracket tend to zero, and we should therefore expect that the asymptotic form of *any* solution G would be

$$G \sim A \sin(kr + \epsilon), \quad (13)$$

where A and ϵ are constants.

To test whether this is so, we set

$$G = u(r)e^{ikr}.$$

† We assume that if $U(r)$ has a pole at the origin, it is not of higher order than r^{-1} . Cf. § 3.

Substituting in (12), we obtain

$$\frac{d^2u}{dr^2} + 2ik \frac{du}{dr} - \left[U + \frac{n(n+1)}{r^2} \right] u = 0. \quad (14)$$

For large r , we may assume, since u is nearly a constant,

$$\frac{d^2u}{dr^2} \ll k \frac{du}{dr}.$$

Neglecting the former term, we can integrate (14); we obtain

$$2ik \log u = \int^r \left[U(r) + \frac{n(n+1)}{r^2} \right] dr.$$

The right-hand side tends to a constant for large r if and only if $U(r)$ tends to zero faster than $1/r$ as r tends to infinity. Thus for fields which fall to zero faster than the Coulomb field, G has the asymptotic form (13). The case of the Coulomb field is considered in Chapter III.

The particular solution of (11) that is finite at the origin will therefore have the form

$$Cr^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n),$$

where C is an arbitrary constant, and † η_n is a constant that depends on k and on $U(r)$, and which can in general only be determined by numerical integration (cf. § 3). To fix the arbitrary constant C , we define $L_n(r)$ to be that bounded solution of (11) that has the asymptotic form

$$(kr)^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n). \quad (15)$$

We have to choose the constants A_n in (10). If we subtract the expression (8) for the incident plane wave, we obtain the expression for the scattered wave. We have to choose the A_n so that this does actually represent a scattered wave—i.e. so that there are no terms of the type $r^{-1}e^{-ikr}$ in the asymptotic expansion. Thus for all n we must have, for large r ,

$$A_n L_n(r) - (2n+1)i^n f_n(r) \sim C_n r^{-1} e^{ikr},$$

where C_n is some constant. Putting in the asymptotic expressions for L_n, f_n , we obtain for the left-hand side

$$\frac{e^{ik\rho}}{2ikr} [A_n e^{i\eta_n} - (2n+1)i^n] - \frac{e^{-ik\rho}}{2ikr} [A_n e^{-i\eta_n} - (2n+1)i^n],$$

where

$$k\rho = kr - \frac{1}{2}n\pi.$$

Choosing A_n so that the second term shall vanish, we have

$$A_n = (2n+1)i^n e^{i\eta_n}.$$

† The term $-\frac{1}{2}n\pi$ is added so that, if $U(r)$ is zero, η_n shall be zero.

For the wave function, therefore, that represents the incident wave and the scattered wave, we have

$$\psi = \sum_{n=0}^{\infty} (2n+1) i^n e^{i\eta_n} L_n(r) P_n(\cos \theta), \quad (16)$$

and for the asymptotic form of the scattered wave

$$r^{-1} e^{ikr} f(\theta),$$

with
$$f(\theta) = \frac{1}{2ik} \sum_{n=0}^{\infty} (2n+1) [e^{2i\eta_n} - 1] P_n(\cos \theta). \quad (17)$$

This gives us our expression for the amplitude of the scattered wave. It will be noticed that $f(\theta)$ is complex; the scattered intensity $I(\theta)$ is given by the square of the modulus, i.e. by $A^2 + B^2$, where

$$A = \frac{1}{2k} \sum (2n+1) [\cos 2\eta_n - 1] P_n,$$

$$B = \frac{1}{2k} \sum (2n+1) \sin 2\eta_n P_n.$$

These series are, in general, convergent (cf. § 2). There is only one case in which the series (17) can be summed in terms of known functions, namely, the scattering by a Coulomb field, which we shall consider in Chapter III. We shall find there that the scattered intensity is the same as that given by the classical theory. This is not true of any other field that has been investigated.

The *total elastic cross-section* Q of an atom for electrons of a given velocity is defined as the total number of electrons scattered elastically by the atom, per unit time, from a beam of unit intensity, i.e. such that one electron crosses unit area per unit time. In practice the number scattered through an angle greater than some small angle θ_0 is measured, but since $f(\theta)$ is bounded at $\theta = 0$ for atomic fields, Q is very insensitive to θ_0 , and thus θ_0 may be taken to be zero.†

The formula for Q is

$$Q = 2\pi \int_0^\pi |f(\theta)|^2 \sin \theta \, d\theta.$$

This gives

$$Q = \frac{4\pi}{k^2} \sum_{n=0}^{\infty} (2n+1) \sin^2 \eta_n. \quad (18)$$

The method of this section was first used by Rayleigh.‡ It was first applied to the problem of the scattering of electrons by atoms by Faxén and Holtmark.§

† Cf. Chap. X, § 2.

§ *Zeits. f. Physik*, 45 (1927), 307.

‡ *Theory of Sound*, ii. 323.

2. Connexion between the phases η_n and the angular momentum of the scattered particle

The phases η_n that occur in the expression (17) for the scattered amplitude are, as we have seen, defined in the following way. Let $G_n(r)$ be the bounded solution of

$$G'' + \left[k^2 - U(r) - \frac{n(n+1)}{r^2} \right] G = 0, \quad (19)$$

where the dashes denote differentiation with respect to r . Then, for large r , G will have the asymptotic form

$$G \sim \sin(kr - \frac{1}{2}n\pi + \eta_n);$$

η_n is thus defined.

If $U(r)$ falls exponentially to zero for large r , it is possible to make an estimate of the value of η_n for fairly large n , and thus to estimate the number of terms required to sum the series (17) for $f(\theta)$. The convergence of the series may also be tested in this way.

Let us denote by $F(r)$ the function

$$F(r) = k^2 - U(r) - \frac{n(n+1)}{r^2}. \quad (20)$$

If $U(r)$ has no pole of higher order than r^{-1} , $F(r)$ is negative for small r and positive for large r , and has therefore at least one zero. For simplicity we shall suppose that $F(r)$ has only one zero, which we call r_n .

The solution G of equation (19) behaves for small r like $A r^{n+1}$, where A is a constant which we shall assume positive. Thus for small r , both G and G' are positive, and we see from (19) that G'' is positive also. Now, for increasing r , G cannot decrease until G' changes sign, and this can only happen for a value of r greater than the first zero of G'' . But since G is increasing and therefore positive until the first zero of G'' , it follows from (19) that this zero is at the point r_n . Thus G increases (exponentially) until the point $r = r_n$. The proof is similar if A is negative.

For $r > r_n$, G is an oscillating function, as shown in Fig. 2.

Let us now find the closest distance of approach, according to the classical theory, of an electron of energy E fired at an atom, in such a way that its angular momentum about the nucleus is I . I is the product of the initial momentum of the electron and the 'impact parameter'† p . If v be the velocity of the electron at the point of closest

† The 'impact parameter' is the distance between the initial line of motion of the particle and the centre of the scattering field.

approach, we have, firstly, since energy is conserved,

$$\frac{1}{2}mv^2 + V(r) = E,$$

and secondly, by the principle of conservation of angular momentum, since the radial velocity is zero at the point of closest approach,

$$mvr = I.$$

Eliminating v , we obtain for r the equation

$$E - V(r) - I^2/2mr^2 = 0. \quad (21)$$

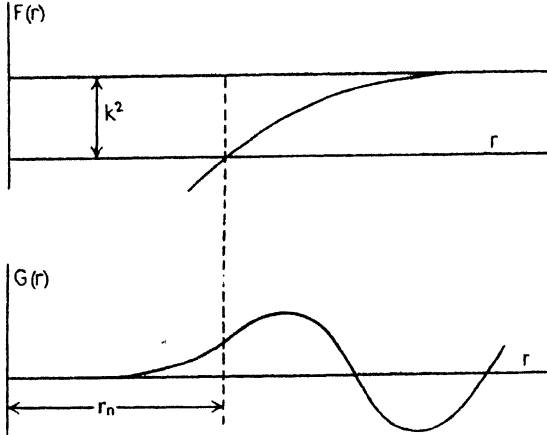


FIG. 2

If we put

$$I = h[n(n+1)]^{1/2}/2\pi, \quad (22)$$

then equation (21) is equivalent to

$$F(r) = 0,$$

$F(r)$ being defined by (20). Thus the zero r_n of $F(r)$ is the distance to which a particle of angular momentum given by (22) would approach, according to the classical theory.

We have already seen that $|G_n(r)|$ is very small for r much less than r_n . We shall now show that if n is so big that a particle with angular momentum I given by (22) does not penetrate the atom (according to the classical theory), then the corresponding phase η_n is very small. We have to show, therefore, that if $V(r_n)$ is very small for n greater than a certain value, η_n is also very small for these values of n . We note that if $V(r_n)$ is very small, r_n is approximately the zero of

$$k^2 - n(n+1)/r^2.$$

Let now $g_n(r)$ be that solution of the equation

$$\frac{d^2g}{dr^2} + \left\{ k^2 - \frac{n(n+1)}{r^2} \right\} g = 0 \quad (23)$$

which is bounded at the origin, the arbitrary multiplying constant being chosen in such a way that

$$g_n \sim \sin(kr - \frac{1}{2}n\pi)$$

for large r . g_n is equal to†

$$(\pi kr/2)^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr).$$

It follows from the arguments given above that g_n decreases exponentially as r decreases, for r less than r_n . The form of the function is similar to that of the function G illustrated in Fig. 2.

We now solve the wave equation (19) by a perturbation method. We put

$$G_n = g_n + \Phi$$

and assume that the product ΦU can be neglected. Substituting into the equation (19), we obtain for Φ ,

$$\frac{d^2\Phi}{dr^2} + \left\{ k^2 - \frac{n(n+1)}{r^2} \right\} \Phi = U(r)g_n(r). \quad (24)$$

Let

$$\Phi = g_n(r)\zeta(r).$$

Then, substituting in (24), we obtain

$$\zeta''g_n + 2\zeta'g'_n = U(r)g_n(r).$$

Multiplying this equation by $g(r)$, and integrating, we obtain

$$\zeta'g^2 = \int^r U(r)[g(r)]^2 dr.$$

Since ζ' must be bounded at $r = 0$, and $g(r)$ behaves like r^{n+1} for small r , the lower limit of integration must be zero. Thus we see that

$$\frac{d\zeta}{dr} = [g(r)]^{-2} \int_0^r U(r)[g(r)]^2 dr.$$

For large r we have therefore

$$\frac{d\zeta}{dr} \sim \operatorname{cosec}^2(kr - \frac{1}{2}n\pi) \int_0^\infty U(r)[g(r)]^2 dr, \quad (25)$$

since the integral on the right converges.

Let us denote by A_n the integral

$$\int_0^\infty U(r)[g_n(r)]^2 dr.$$

We have postulated that, for the value of n considered, $U(r)$ is small for $r > r_n$, and we know that g_n is small for $r < r_n$. Thus A_n is small.

† Cf. equation (9).

Integrating (25), we obtain

$$\zeta \sim -[\cot(kr - \frac{1}{2}n\pi) + \alpha]A_n/k,$$

where α is a constant. Hence we obtain

$$G_n \sim \sin(kr - \frac{1}{2}n\pi) - [\cos(kr - \frac{1}{2}n\pi) + \alpha \sin(kr - \frac{1}{2}n\pi)]A_n/k.$$

Neglecting terms involving the square of η_n , we see that

$$G_n \sim \text{const.} \sin(kr - \frac{1}{2}n\pi + \eta_n), \quad (26)$$

where

$$\eta_n = -A_n/k.$$

Writing out this formula for η_n in full, we obtain

$$\eta_n = -\frac{1}{2}\pi \frac{8\pi^2 m}{\hbar^2} \int_0^\infty V(r) [J_{n+\frac{1}{2}}(kr)]^2 r \, dr. \quad (27)$$

The formula is valid if the right-hand side is small, and shows that η_n is small under the conditions stated.

The formula (27), being valid for large n , may be used to test the convergency of series (17) for the scattered amplitude. The series converges if

$$\sum \eta_n P_n(\cos \theta)(2n+1)$$

converges.

If $\eta_n \ll 1$ for all n , the formula (27) may be used for all n . We then obtain for the scattered amplitude

$$f(\theta) = \frac{1}{k} \sum_{n=0}^{\infty} (2n+1) \eta_n P_n(\cos \theta). \quad (28)$$

The series may be summed and yields the well-known Born formula (cf. Chap. VII, § 2).

3. Scattering by a potential hole

In this section we illustrate the theory by the important case of scattering by a potential hole.

We take for the potential of the particle in the scattering field

$$\begin{aligned} V(r) &= -D & (r < a), \\ &= 0 & (r > a), \end{aligned}$$

where D is a positive constant. This simple case includes a great number of features common to scattering by attractive potentials in general, provided they fall off more rapidly than r^{-2} for large r . We shall therefore use it as one example to illustrate the theory.

3.1. *Low-velocity limit of the cross-section.*

We shall first suppose that the wave-length λ is very much greater than a , so that all the phases η_n are negligible except the first, η_0 . (Note that the distance of closest approach of a particle with one quantum of angular momentum is $\lambda/2\pi$ if the particle does not enter the potential

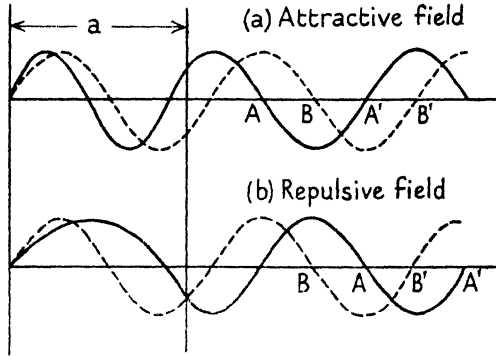


FIG. 3

hole.) To obtain η_0 we have to find the asymptotic form of the solution of

$$\frac{d^2G}{dr^2} + \frac{8\pi^2m}{h^2} (E - V)G = 0,$$

which vanishes at the origin (since $r^{-1}G$ must be bounded). The solution is

$$\begin{aligned} A \sin k'r & \quad (r < a), \\ \sin(kr + \eta_0) & \quad (r > a), \end{aligned}$$

where

$$k^2 = 8\pi^2mE/h^2, \quad k'^2 = k^2 + k_0^2, \quad k_0^2 = 8\pi^2mD/h^2.$$

The constants A and η_0 must be chosen in such a way that G and dG/dr are continuous at $r = a$; i.e. in such a way that

$$\begin{aligned} A \sin k'a & = \sin(ka + \eta_0), \\ Ak' \cos k'a & = k \cos(ka + \eta_0). \end{aligned}$$

These two equations give us

$$\eta_0 = \tan^{-1}\left(\frac{k}{k'} \tan k'a\right) - ka. \tag{29}$$

In Fig. 3(a) the wave function G is shown by the full line; the dotted line represents the curve $G = \sin kr$.

The phase η_0 is represented by the length AB , or $A'B'$, multiplied by k .

It will be seen from the figure that η_0 is positive for an attractive field; for a repulsive field η_0 is negative, as will be shown below.

As the velocity of the particles tends to zero η_0 , in general, tends to zero also, as may be seen from equation (29). The scattering cross-section, $4\pi \sin^2 \eta_0 / k^2$, tends to the finite limit

$$4\pi a^2 \left(\frac{\tan k_0 a}{k_0 a} - 1 \right)^2. \quad (30)$$

There are exceptional cases, however. If $k_0 a = \tan k_0 a$ the limit

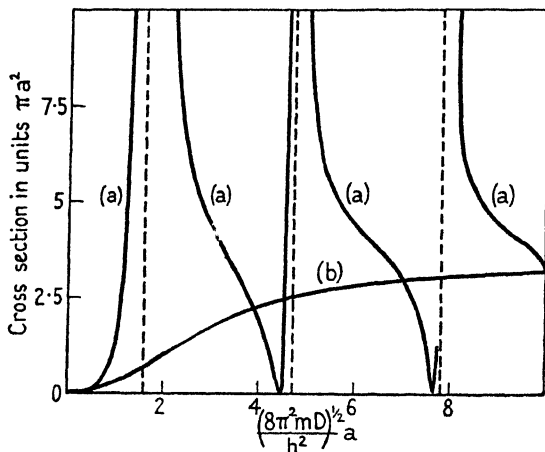


FIG. 4. Low-velocity limit of the collision cross-section as a function of the strength of the field

(a) For spherical wells of depth D and radius a .

(b) For spherical potential barriers of height D and radius a .

vanishes, while if $k_0 a$ is an odd multiple of $\frac{1}{2}\pi$, η_0 does not tend to zero with k and the scattering cross-section tends to infinity. Hence, if we consider the low-velocity limit of the effective scattering cross-section of the potential hole as a function of k_0 , that is to say, of the square root of its depth, we obtain the curve illustrated in Fig. 4.

This behaviour of the low-velocity limit of the cross-section may be related to the distribution of allowed energy levels, with zero angular momentum, within the hole. In order that a level of energy $-E_1$ should exist, we must have

$$A \sin k'' a = e^{-\kappa a},$$

$$A k'' \cos k'' a = -\kappa e^{-\kappa a},$$

where now

$$\kappa^2 = 8\pi^2 m E_1 / h^2, \quad k''^2 = k_0^2 - \kappa^2.$$

This requires that

$$\frac{\tan k'' a}{k'' a} = -\frac{1}{\kappa}, \quad (31)$$

the roots κ of which determine the energy-levels. The condition that $E_1 = 0$ should be an energy-level is that $k_0 a$ should be an odd multiple of $\frac{1}{2}\pi$, the same as that for the existence of an unbounded low-velocity limit for the collision cross-section. The successive infinite discontinuities in Fig. 4(a) correspond respectively to increasing numbers of allowed energy-levels in addition to the one at zero energy. Thus when $k_0 a = \frac{1}{2}\pi$ there is only one allowed energy-level, that for $E_1 = 0$, but when $k_0 a = 3\pi/2$ there are two energy-levels, the upper of which has $E_1 = 0$, and so on.

The same quasi-periodic and singular behaviour of the scattering cross-section in the limit of low velocities occurs with attractive potentials in general. It is possible, therefore, that the cross-section of an atom for very slow electrons may be either much smaller or much larger than the region in which $V(r)$ is comparable with the energy of the electron. Examples of this will be discussed in Chap. X, §§ 3 and 4. Another important practical case is that of the scattering of neutrons by protons, which is considered in detail in Chap. XIII, § 1.

3.2. Velocity variation of η_0 and of the zero-order partial cross-section

We have
$$\lim_{k \rightarrow 0} \eta_0 = \lim_{k \rightarrow 0} \left\{ \tan^{-1} \left(\frac{k}{k'} \tan k' a \right) - ka \right\}.$$

This limit is indefinite by an integral multiple of π . Thus

$$\begin{aligned} \lim_{k \rightarrow 0} \eta_0 &= s\pi & (s = 0, 1, 2, \dots), & & k_0 a \neq \frac{1}{2}\pi \\ &= \frac{1}{2}(2s+1)\pi & (s = 0, 1, 2, \dots), & & k_0 a = \frac{1}{2}\pi. \end{aligned}$$

It is convenient to remove this many-valuedness by specifying that η_0 should tend to zero as the velocity, and hence k , tends to ∞ .

With the formula (27) we have, for large k ,

$$\eta_0 \rightarrow \frac{1}{2}k_0^2 a/k,$$

tending to zero at very large velocities. If we allow η_0 to change continuously as k decreases we find that as $k \rightarrow 0$, η_0 tends to the nearest whole multiple of π below $k_0 a$, i.e. to a multiple of π equal to the number of energy-levels with zero angular momentum which exist in the potential hole. Exceptions arise only when $k_0 a$ is a half-integral multiple of $\frac{1}{2}\pi$, in which case η_0 tends to $k_0 a$. Fig. 5(a) illustrates the variation of η_0 with k for three typical cases in which there exist zero, one, and two such energy-levels.

Turning now to the velocity variation of the zero-order partial cross-section $Q_0 = 4\pi \sin^2 \eta_0 / k^2$, we see that, if the low-velocity limit of η_0

is $s\pi$, where s is greater than 2, then Q_0 must vanish for such values of k that $\eta_0 = (s-1)\pi, (s-2)\pi, \dots$, etc. The physical significance of these vanishing cross-sections is that, for such values of k , the potential hole

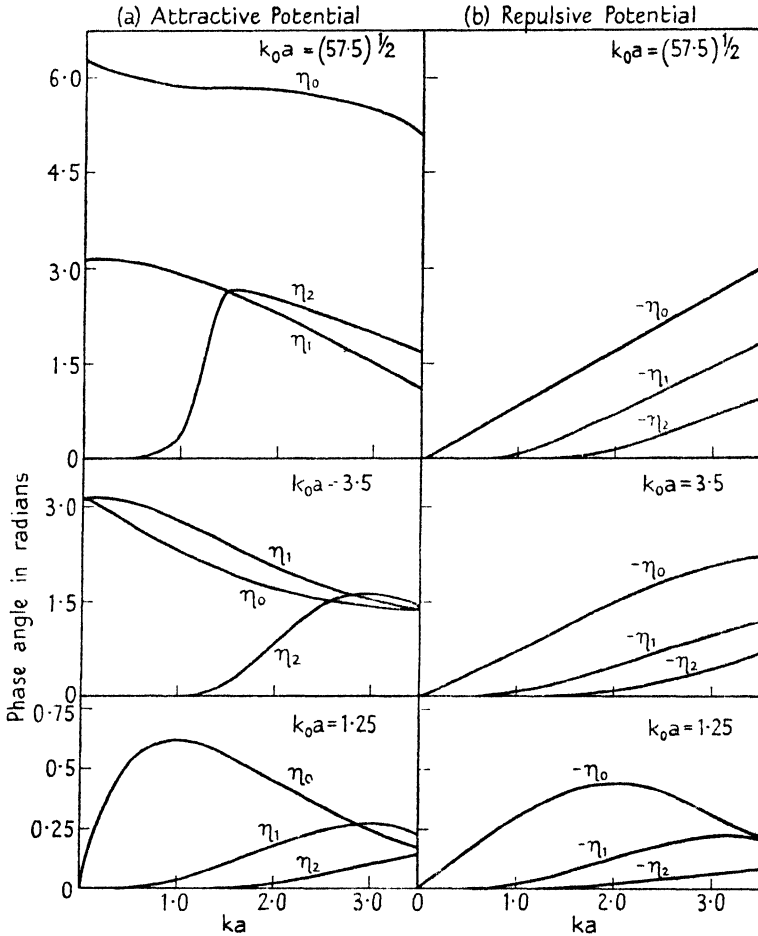


FIG. 5. Variation of phases η_0, η_1, η_2 with velocity for different strengths of field

(a) For spherical wells of depth $D \left(= \frac{k_0^2 \hbar^2}{2m} \right)$ and radius a .

(b) For spherical potential barriers of height $D \left(= \frac{k_0^2 \hbar^2}{2m} \right)$ and radius a .

is just strong enough to introduce one or more additional complete wave-lengths within its range of action. To all intents and purposes the wave outside the hole remains unaffected, the gain of one or more complete wave-lengths being unobservable at infinity.

If Q_0 passes through a zero at some finite value of k for which the

first- and higher-order cross-sections are still very small, the total cross-section Q will show a deep minimum at this particular velocity. This possibility exists for scattering by attractive fields in general and is responsible for the Ramsauer-Townsend effect in the scattering of electrons by certain atoms (see Chap. X). Typical variations of Q_0 with velocity are illustrated in Fig. 6 a.

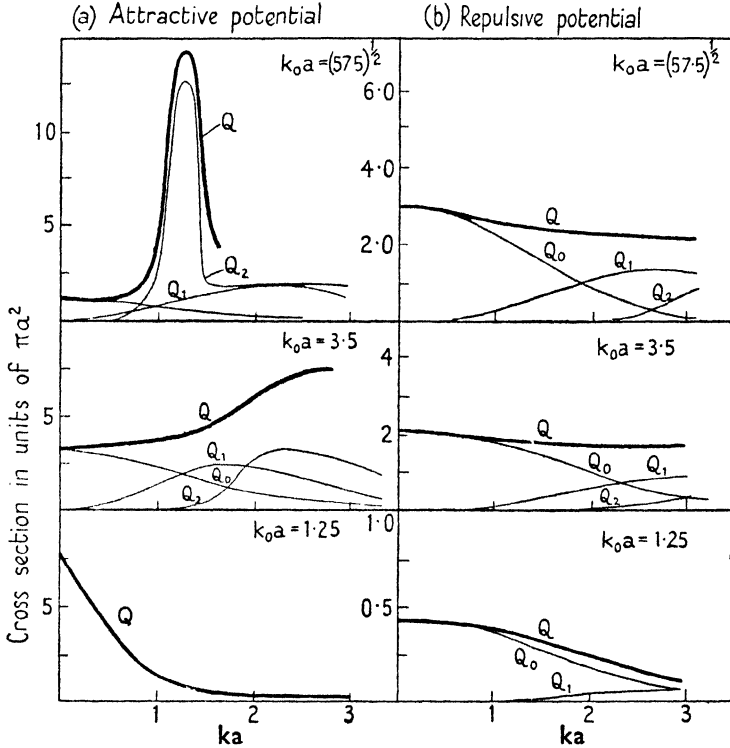


FIG. 6. Variation of partial and total cross-sections Q_0, Q_1, Q_2, Q with velocity for different strengths of field.

(a) For spherical wells of depth $D \left(= \frac{k_0^2 \hbar^2}{2m} \right)$ and radius a .

(b) For spherical potential barriers of height $D \left(= \frac{k_0^2 \hbar^2}{2m} \right)$ and radius a .

Under certain circumstances of importance a useful approximate formula may be obtained for Q_0 .† We consider a deep and narrow potential hole. It is such that

(a) a level exists with binding energy $\frac{\kappa^2 \hbar^2}{2m}$,

(b) $\kappa a \ll 1$. Since $k_0 a > \frac{1}{2}\pi$ in order that an energy level should exist,

† Wigner, *Zeits. f. Physik*, 83 (1933), 253.

it follows that $k_0 \gg \kappa$, i.e. that the binding energy is small compared with the depth of the hole.

We now obtain an approximate expression for Q_0 for such velocities that $ka \ll 1$. To do this we expand

$$\sin^2 \eta_0 = \sin^2 \left\{ \tan^{-1} \left(\frac{k}{k'} \tan k'a \right) - ka \right\},$$

in powers of $(k^2 + \kappa^2)/(k_0^2 - \kappa^2)$, using the relation

$$\frac{\tan\{(k_0^2 - \kappa^2)^{\frac{1}{2}} a\}}{(k_0^2 - \kappa^2)^{\frac{1}{2}}} = -\frac{1}{\kappa}. \quad (32)$$

We find then that

$$Q_0 = \frac{4\pi}{k^2 + \kappa^2} (1 + \kappa a + \text{terms of higher order}). \quad (33)$$

The equation (32) has a root κ satisfying the condition (b) if $k_0 a$ is slightly greater than $\frac{1}{2}\pi$. If, on the other hand, $k_0 a$ is slightly less than $\frac{1}{2}\pi$, a quantity $\lambda \ll k_0$ can be found which satisfies

$$\frac{\tan\{(k_0^2 + \lambda^2)^{\frac{1}{2}} a\}}{(k_0^2 + \lambda^2)^{\frac{1}{2}}} = \frac{1}{\lambda}. \quad (34)$$

Q_0 may then be written

$$Q_0 = \frac{4\pi}{k^2 + \lambda^2} (1 - \lambda a + \text{terms of higher order}). \quad (35)$$

In this case no real energy level exists but only a virtual one.†

Under the conditions we have specified the velocity variation of the cross-section gives direct information about the real or virtual energy of the level nearest to zero. (All partial cross-sections except Q_0 will be negligible for $ka \ll 1$.) It is important to remember, however, that there is no means of telling whether the level is real or virtual, without having recourse to some other type of measurement.

The application of the formulæ (33) and (35), which do not depend on the detailed shape of the potential field provided its range is small, to the interaction between neutron and proton is discussed in Chap. XIII, § 1.1.

† At a virtual level for which λa is small, λ is nearly equal to the value of k for which the phase-shift $\eta_0 = \frac{1}{2}\pi$ (Breit, Thaxton, and Eisenbud, *Phys. Rev.* **55** (1939), 1018; Plesset and Brown, *Proc. Nat. Acad. Sci.* **25** (1939), 600). Another definition has been given by Hulthén, *Arkiv. Math. Ast. Phys.*, *Svenska Vet. Akad.* **29** (1942), which agrees with (34) for the case of a spherical well interaction when $\lambda a \ll \frac{1}{2}\pi$.

3.3. *The higher order phases and partial cross-sections*

To determine η_n we must find the asymptotic form of the solution of

$$\frac{d^2G}{dr^2} + \left[k'^2 - \frac{n(n+1)}{r^2} \right] G = 0 \quad (r < a),$$

$$\frac{d^2G}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} \right] G = 0 \quad (r > a),$$

which vanishes at the origin. The solution is

$$Ar^{\frac{1}{2}}J_{n+\frac{1}{2}}(k'r) \quad (r < a),$$

$$\left(\frac{1}{2}\pi kr\right)^{\frac{1}{2}}[\cos \eta_n J_{n+\frac{1}{2}}(kr) + (-1)^n \sin \eta_n J_{-n-\frac{1}{2}}(kr)] \quad (r > a).$$

This follows from the fact that†

$$J_{n+\frac{1}{2}}(kr) \sim \left(\frac{2}{\pi kr}\right)^{\frac{1}{2}} \sin(kr - \frac{1}{2}n\pi),$$

$$J_{-n-\frac{1}{2}}(kr) \sim (-1)^n \left(\frac{2}{\pi kr}\right)^{\frac{1}{2}} \cos(kr - \frac{1}{2}n\pi).$$

Using the condition of continuity of G and dG/dr at $r = a$ we find

$$\tan \eta_n = (-1)^{n-1} A_n/B_n,$$

where

$$\left. \begin{aligned} A_n &= kJ_{n+\frac{1}{2}}(k'a)J'_{n+\frac{1}{2}}(ka) - k'J_{n+\frac{1}{2}}(ka)J'_{n+\frac{1}{2}}(k'a), \\ B_n &= kJ_{n+\frac{1}{2}}(k'a)J'_{-n-\frac{1}{2}}(ka) - k'J_{-n-\frac{1}{2}}(ka)J'_{n+\frac{1}{2}}(k'a). \end{aligned} \right\} \quad (36)$$

By making use of the relations‡

$$xJ'_{n+\frac{1}{2}}(x) = xJ_{n-\frac{1}{2}}(x) - (n+\frac{1}{2})J_{n+\frac{1}{2}}(x),$$

$$xJ'_{-n-\frac{1}{2}}(x) = -(n+\frac{1}{2})J_{-n-\frac{1}{2}}(x) - xJ_{-n+\frac{1}{2}}(x),$$

this may be thrown into the alternative form

$$\tan \eta_n = (-1)^n C_n/D_n,$$

where

$$\left. \begin{aligned} C_n &= kJ_{n+\frac{1}{2}}(k'a)J_{n-\frac{1}{2}}(ka) - k'J_{n+\frac{1}{2}}(ka)J_{n-\frac{1}{2}}(k'a), \\ D_n &= kJ_{n+\frac{1}{2}}(k'a)J_{-n+\frac{1}{2}}(ka) + k'J_{-n-\frac{1}{2}}(ka)J_{n-\frac{1}{2}}(k'a). \end{aligned} \right\} \quad (37)$$

To examine the behaviour with particle velocity we make use of the approximations for small x §

$$J_{n+\frac{1}{2}}(x) = \left(\frac{2x}{\pi}\right)^{\frac{1}{2}} \frac{(2x)^{nn!}}{(2n+1)!},$$

$$J_{-n-\frac{1}{2}}(x) = \left(\frac{2x}{\pi}\right)^{\frac{1}{2}} \frac{(2x)^{-n-12}(2n)!}{n!} (-1)^n \left(1 + \frac{x^2}{4n-2}\right).$$

This gives, for small ka ,

$\tan \eta_n$

$$= \frac{n!(n-1)!}{4(2n+1)!(2n-1)!} [(2n+1)f_n - 1] \left[1 - \frac{k^2 a^2}{2n-1} (f_n - \frac{1}{2}) \right]^{-1} (2ka)^{2n+1},$$

where

$$f_n = J_{n+\frac{1}{2}}(k'a) / \{k'a J_{-n-\frac{1}{2}}(k'a)\}.$$

† Whittaker and Watson, *Modern Analysis* (Cambridge, 1927), 4th edition, Chap. XVII, 365.

‡ *Ibid.*, p. 360.

§ *Ibid.*, p. 355.

Hence, if $J_{n-\frac{1}{2}}(k_0 a) \neq 0$, we have

$$\lim_{k \rightarrow 0} \eta_n = \frac{n!(n-1)!}{4(2n+1)!(2n-1)!} [(2n+1)f_n(0) - 1] (2ka)^{2n+1} + s\pi \quad (s = 0, 1, 2, \dots),$$

where $f_n(0) = J_{n+\frac{1}{2}}(k_0 a) / \{k_0 a J_{n-\frac{1}{2}}(k_0 a)\}$. (38)

If $J_{n-\frac{1}{2}}(k_0 a) = 0$,

$$\lim_{k \rightarrow 0} \eta_n = - \frac{n!(n-1)!}{(2n)!(2n-2)!} (2ka)^{2n-1} + s\pi \quad (s = 0, 1, 2, \dots). \quad (39)$$

Comparing the behaviour of these phases with that of η_0 , we notice certain points of similarity. The special case $J_{n-\frac{1}{2}}(k_0 a) = 0$, which gives a slower dependence on velocity, corresponds to the existence of a level of zero energy with angular momentum $\{n(n+1)\}^{\frac{1}{2}}\hbar$. If we adopt the convention that η_n should tend to zero for large velocities, then the value of s in (38) and (39) is determined, as for η_0 , as being the number of energy levels with angular momentum $\{n(n+1)\}^{\frac{1}{2}}\hbar$. This number can never increase as n increases, since the acquirement of extra angular momentum leads, owing to the extra centrifugal force, to a weakening of the binding.

If ka is small the importance of the successive phases falls off rapidly as n increases. Typical sets of phase-velocity curves are illustrated in Fig. 5(a).

Turning now to the partial cross-sections $Q_n = 4\pi(2n+1)\sin^2\eta_n/k^2$, we see from (38) and (39) that, for all $n > 0$, Q_n never tends to ∞ as $k \rightarrow 0$. In fact for $n > 1$, Q_n must always tend to 0 at least as fast as k^{4n-4} and usually as k^{4n} . It is only in the special case of $n = 1$ and $J_{\frac{1}{2}}(k_0 a) = 0$ that Q_n tends to a finite value as $k \rightarrow 0$. For this case we find, using the explicit expression

$$J_{\frac{1}{2}}(x) = \left(\frac{\pi}{2x}\right)^{\frac{1}{2}} \sin x,$$

that

$$\lim_{k \rightarrow 0} Q_1 = 12\pi a^2.$$

As this occurs when $k_0 a$ is an integral multiple of π (other than zero), it arises when $\lim_{k \rightarrow 0} Q_0$ vanishes, so that the low-velocity limit of the total cross-section can never be exactly zero.

Typical sets of cross-section velocity curves are illustrated in Fig. 6(a).

4. Scattering by a uniform potential barrier

We now consider the case where the scattering potential is given by

$$\begin{aligned} V(r) &= D & (r < a), \\ &= 0 & (r > a), \end{aligned}$$

which can be regarded as exemplifying repulsive potentials in general which fall off more rapidly than r^{-2} for large r . The case of an impenetrable sphere, for which D tends to infinity, is also a rather special one and will be discussed separately in the next section.

We have, writing $k'^2 = k_0^2 \sim k^2$, where $k_0^2 = 8\pi^2mD/h^2$,

$$\begin{aligned}\eta_0 &= \tan^{-1}\left(\frac{k}{k'} \tanh k'a\right) - ka & (k < k_0), \\ &= \tan^{-1}\left(\frac{k}{k'} \tan k'a\right) - ka & (k > k_0).\end{aligned}\quad (40)$$

The wave function is illustrated in Fig. 3(b) and compared with the curve $G = \sin kr$. The phase η_0 , represented by the length AB multiplied by k , is negative.

In the limit of low velocities η_0 tends to zero, no matter what the value of D may be. The scattering cross-section tends to the finite limit

$$4\pi a^2 \left(\frac{\tanh k_0 a}{k_0 a} - 1 \right)^2, \quad (41)$$

which is always less than $4\pi a^2$, a value to which it tends as D becomes very large. This is in sharp contrast with the case of the potential well discussed in the preceding section. The anomalous behaviour of the scattering cross-section in that case was shown to be related to the existence of energy levels in the well. No such energy levels can exist in the repulsive field and no anomalies arise in the scattering cross-section. The variation of the low-velocity limit of the cross-section with $k_0 a$ is illustrated in Fig. 4.

Considering again the relation between the number of energy levels and the integral multiple of π to which the phase tends as the velocity tends to zero, we would expect for the repulsive field, in which no energy levels exist, that the phase η_0 should always tend to zero for both large and small velocities. This is indeed the case, as may be seen from Fig. 5(b). On the other hand, η_0 may pass through values of $s\pi$, where s is a negative integer, at intermediate values of the velocity. At such points the zero-order partial cross-section vanishes—the potential barrier produces no observable effect at great distances on the waves of zero angular momentum because it just *eliminates* a whole number s complete waves which in its absence would have occurred in the distance a . This can only arise if the asymptotic wave-length is smaller than a , under which conditions the higher order partial cross-sections cannot be neglected. It is therefore not to be expected that the *total*

cross-section due to a repulsive field can ever show a deep minimum as a function of velocity. This is in contrast to the potential well, which can introduce additional waves in a region shorter than a wave-length, so that conditions may arise in which all the higher order partial cross-sections are small at a velocity for which that of zero-order vanishes.

The phase η_n is given, for $k < k_0$, by

$$\tan \eta_n = (-1)^n C_n / D_n,$$

where

$$\left. \begin{aligned} C_n &= k I_{n+\frac{1}{2}}(k'a) J_{n-\frac{1}{2}}(ka) - k' J_{n+\frac{1}{2}}(ka) I_{n-\frac{1}{2}}(k'a), \\ D_n &= k I_{n+\frac{1}{2}}(k'a) J_{-n+\frac{1}{2}}(ka) + k' J_{-n+\frac{1}{2}}(ka) I_{n-\frac{1}{2}}(k'a). \end{aligned} \right\} \quad (42)$$

$I_{n+\frac{1}{2}}(x)$ is the Bessel function defined by

$$I_{n+\frac{1}{2}}(x) = i^{-(n+\frac{1}{2})} J_{n+\frac{1}{2}}(ix).$$

For $k > k_0$, $I_{n+\frac{1}{2}}(k'a)$ is replaced by $J_{n+\frac{1}{2}}(k'a)$.

We now have

$$\lim_{k \rightarrow 0} \eta_n = \frac{n!(n-i)!}{4(2n+1)!(2n-1)!} [(2n+1)f_n(0) - 1] (2ka)^{2n+1},$$

where

$$f_n(0) = I_{n+\frac{1}{2}}(k_0 a) / \{k_0 a I_{n-\frac{1}{2}}(k_0 a)\}.$$

As $I_{n-\frac{1}{2}}(k_0 a)$ does not vanish except when $k_0 = 0$, there are no special cases. This is expected from the absence of energy levels of any angular momentum. Just as for η_0 , $\eta_n \rightarrow 0$ as $k \rightarrow 0$ and $k \rightarrow \infty$.

Typical sets of phase velocity and cross-section velocity curves are illustrated in Figs. 5(b), 6(b) respectively.

5. Scattering by an impenetrable sphere

This represents the limiting case of the preceding example when $D \rightarrow \infty$. The wave function G must vanish at the boundary of the sphere so we have, for $n = 0$,

$$G = \sin k(r-a),$$

giving $\eta_0 = -ka$, a result which might have been derived by making $k' \rightarrow \infty$ in (40).

For the higher order phases

$$\tan \eta_n = (-1)^{n-1} \frac{J_{n+\frac{1}{2}}(ka)}{J_{-n-\frac{1}{2}}(ka)}. \quad (43)$$

The low-velocity limit of the cross-section is $4\pi a^2$, four times the classical value. It is of interest to note that, even at the highest velocities, the classical value is not approached, but a value twice as great. This may be seen as follows.

For values of ka large compared with n , we may replace the Bessel functions in (43) by their asymptotic values to give

$$\eta_n = -ka - \frac{1}{2}n\pi. \tag{44}$$

The sum of the partial cross-sections for $n < ka$ may now be replaced by the integral

$$\begin{aligned} \frac{4\pi}{k^2} \int_0^{ka} (2x+1) \sin^2(ka - \frac{1}{2}x\pi) dx \\ = 2\pi a^2 + O\left(\frac{1}{ka}\right). \dagger \end{aligned} \tag{45}$$

For $n > ka$ the ratio of the Bessel functions falls off very rapidly, as

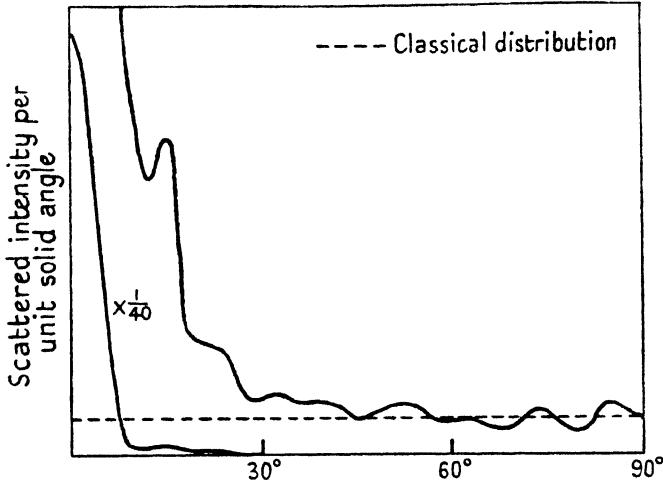


FIG. 7. Angular distribution for scattering by a rigid sphere for the case $ka = 20$.

$(ka/n)^n$, so the contribution of the partial cross-sections, for $n > ka$, may be neglected. We therefore have

$$\lim_{k \rightarrow \infty} Q = 2 \times \text{geometrical cross-section.}$$

This somewhat paradoxical result, first noticed by Massey and Mohr, † arises from the impossibility, due to diffraction, of accurate determination of angles of deflexion below a certain magnitude. There is always a cone of finite angle (of order π/ka), centred at the obstacle and with axis in the incident direction, within which the scattering is non-

† A more precise treatment, using a closer approximation to η_n than (43), shows that the error is actually $O\{(ka)^{-\frac{1}{2}}\}$ (Wergeland, *Skrif. Norske Videns. Akad. Oslo, Mat.-Nat. Klasse*, 1945, no. 9).

‡ *Proc. Roy. Soc. A*, 141 (1933), 434.

classical. Although the angle of this cone decreases indefinitely with k , the scattered current within it remains at least equal to that distributed, more or less uniformly, throughout the remainder of the angular range. As the latter approximates to the classical scattering it follows that the total scattering is double the classical value. As an illustration, Fig. 7 shows the function $I(\theta)$, calculated for the case $ka = 20$, compared with the uniform classical distribution.

For further details concerning the scattering by impenetrable spheres, reference may be made to the original papers.† Some applications to gas kinetics are referred to in Chap. XII, § 3.1.

6. Scattering by an inverse cube law field

Let the potential energy at distance r from the nucleus be γr^{-2} . Then the wave equation to determine L is

$$\frac{d^2L}{dr^2} + \frac{2}{r} \frac{dL}{dr} + \left\{ k^2 - \frac{n(n+1)}{r^2} \right\} L = 0, \quad \beta = 8\pi^2 m \gamma / \hbar^2. \quad (46)$$

The solutions of this equation are

$$r^{-\frac{1}{2}} J_{\nu+\frac{1}{2}}(kr), \quad (47)$$

where ν is either root of

$$\nu(\nu+1) = n(n+1) + \beta,$$

$$\text{i.e.} \quad \nu = \frac{1}{2}[-1 \pm (1 + 4n + 4n^2 + 4\beta)^{\frac{1}{2}}]. \quad (48)$$

Now our wave function $L(r)$ must be finite at the origin. That is to say, since $r^{-\frac{1}{2}} J_{\nu+\frac{1}{2}}(kr)$ behaves like r^ν at the origin we must have

$$\nu \geq 0 \quad (\text{all } n).$$

If β is positive (repulsive field), then this condition is satisfied for one root and not the other. Thus the bounded solution is unique, as it is for fields with a lower singularity. If β is negative (attractive field), there are then two possibilities; if $-\frac{1}{4} < \beta < 0$ then, for $n = 0$, both solutions are unbounded at the origin, but there is one solution for which the singularity is of a lower order than for any other solution. If we choose to take this as our solution, a formula for the scattered intensity may be obtained. If, on the other hand, $\beta < -\frac{1}{4}$, both solutions behave like $r^{-\frac{1}{2}} \exp(\pm i\alpha \log r)$ near the origin. *There is therefore no solution of the scattering problem for this case.* It is not merely that a singularity of this type at the origin is objectionable. There is no

† Massey and Mohr, loc. cit.; Wergeland, loc. cit.; *Kgl. Dansk. Vidensk. Selskab*, **23** (1945), 14.

solution because there is no criterion as to which solution of equation (46) ought to be taken, and thus the phase η_0 cannot be defined.

Returning to the case of the repulsive field, we see from the asymptotic form of (47) that

$$\eta_n = \frac{1}{2}\pi(\nu - n),$$

where ν is the positive root of equation (48). For large n this reduces to

$$\frac{1}{2}\pi\beta/(2n + 1).$$

The reader will easily verify that formula (27) gives the same result.

As the phase shifts do not depend on the velocity, the angular distribution function $I(\theta)$ retains the same shape at all velocities, in sharp contrast to the cases discussed in the preceding sections. Owing to the slow convergence of the phases η_n for large n , the series of partial cross-sections does not converge and no total cross-section exists. This arises from the unbounded behaviour of $I(\theta)$ as $\theta \rightarrow 0$.†

7. Dispersion formula for the scattering cross-section

We give now an alternative formula for the partial cross-section for scattering of particles of given angular momentum, which bears a close resemblance to that describing optical dispersion by a medium containing damped oscillators possessing various natural frequencies. The formula is not of practical importance for single-body problems, but we give it here because it provides a convenient basis for generalization to many-body phenomena, such as nuclear collisions, for which the dispersion effect is all important (see Chap. VIII, § 8.2; Chap. XIII, § 2). We follow the method due to Kapur and Peierls.‡

Consider first the case of particles with zero angular momentum, moving in a potential field wholly contained within a radius a . The equation for the partial wave is

$$\frac{d^2G_0}{dr^2} + [k^2 - U(r)]G_0 = 0,$$

with $U = 0$, $r > a$. Then, for $r > a$,

$$G_0 = I \frac{\sin kr}{k} + S e^{ikr},$$

the first term representing the incident wave, the second the scattered wave. The zero-order partial cross-section is given by

$$4\pi |S|^2 / |I|^2.$$

In order that G_0 and dG_0/dr be continuous at $r = a$

$$I e^{-ika} = \left(\frac{dG_0}{dr} \right)_a - ikG_0(a), \tag{49}$$

$$S = \cos ka G_0(a) - \frac{1}{k} \sin ka \left(\frac{dG_0}{dr} \right)_a. \tag{50}$$

The amplitude I of the incident wave would vanish if

$$\frac{dG}{dr} - ikG = 0 \quad (r = a). \tag{51}$$

† See Chap. VII, § 1.1.

‡ *Proc. Roy. Soc. A*, **166** (1938), 277.

This is not possible for a solution of the equation which is valid over the whole range of r , but we may take (51), together with the condition $G = 0$ at $r = 0$, as boundary conditions at the ends of the finite interval $0 \leq r \leq a$, to define a set of proper functions \mathcal{G}_s and proper values k_s of the equation

$$\frac{d^2 \mathcal{G}_s}{dr^2} + (k_s^2 - U)\mathcal{G}_s = 0, \quad (52)$$

valid within that interval. k_s^2 will, in general, be complex and a function of k . The functions \mathcal{G}_s will form an orthogonal set, so

$$\int_0^a \mathcal{G}_s \mathcal{G}_s' dr = 0 \quad (k_s^2 \neq k_s'^2),$$

and they may be normalized, so

$$\int_0^a |\mathcal{G}_s|^2 dr = 1.$$

We may now obtain an expansion, valid for $0 \leq r \leq a$, for the actual function G_0 which solves the scattering problem, in terms of the \mathcal{G}_s and k_s .† It is true that G_0 does not satisfy the same boundary conditions as the \mathcal{G}_s , but any function $G_0 - \chi$ does, provided that

$$\chi(0) = 0, \quad (53)$$

$$\left(\frac{d\chi}{dr}\right)_a - ik\chi = Ie^{-ika}, \quad (54)$$

and χ is a proper function throughout the range $0 \leq r \leq a$.

Expanding the function in the usual way in terms of the \mathcal{G}_s we find

$$G_0 = \sum a_s \mathcal{G}_s + \chi, \quad (55)$$

where

$$\frac{a_s}{N_s} = \frac{Ie^{-ika}}{k_s^2 - k^2} \mathcal{G}_s(a) - b_s,$$

$$b_s = \int_0^a \mathcal{G}_s \chi dr, \quad (56)$$

$$N_s = \int_0^a \mathcal{G}_s^2 dr.$$

We have then, on substitution in (50) and using (49),

$$S = I \left\{ \sum_s \frac{e^{-2ika} \mathcal{G}_s^2(a)}{N_s(k_s^2 - k^2)} - \frac{1}{k} \sin ka e^{-ika} \right\} + e^{-ika} \chi(a) - \sum_s \frac{b_s}{N_s} e^{-ika} \mathcal{G}_s(a). \quad (57)$$

This formula must hold for all functions χ which satisfy (53) and (54). We may choose χ to make both the last terms of (57) as small as we please, as, for example, by taking

$$\chi = Cr e^{-\alpha(a-r)},$$

choosing C to satisfy the condition at $r = a$ and then making $\alpha \rightarrow \infty$. It is therefore legitimate to ignore all but the terms within the curly bracket, to give for the zero-order partial cross-section

$$4\pi \frac{|S|^2}{|I|^2} = \frac{\pi}{k^2} \left| \sum_s \frac{w_s^2 e^{-2ika}}{N_s(E_s - E - \frac{1}{2}i\Gamma_s)} - 2e^{-ika} \sin ka \right|^2. \quad (58)$$

† The choice of the particular set of functions \mathcal{G}_s for this expansion may seem rather arbitrary, but it is of special significance for the many-body problem (see Chap. VIII, § 8.21).

Here we have written

$$\frac{\hbar^2}{8\pi^2m} k_s^2 = E_s - \frac{1}{2}i\Gamma_s, \quad \frac{\hbar^2}{8\pi^2m} k^2 = E, \quad \text{and} \quad \left(\frac{\hbar^2}{4\pi^2m}\right)^{\frac{1}{2}} \mathcal{G}_s(a) = w_s. \quad (59)$$

We have further, from the differential equation for \mathcal{G}_s ,

$$i\Gamma_s \int_0^a |\mathcal{G}_s|^2 dr = \frac{\hbar^2}{8\pi^2m} \left[\mathcal{G}_s^* \frac{d\mathcal{G}_s}{dr} - \mathcal{G}_s \frac{d\mathcal{G}_s^*}{dr} \right]_0^a.$$

Use of the boundary condition (51) gives

$$\Gamma_s = |w_s|^2 \quad (60)$$

since \mathcal{G}_s vanishes at $r = 0$.

The sum which occurs in (57) is characteristic of dispersion theory for a set of oscillators with energy levels E_s of natural width Γ_s . The remaining term represents the shadow effect of the scattering field and is referred to in nuclear theory as the 'potential' scattering. It is the same as the amplitude that would be scattered by an impenetrable sphere of radius a .

This analysis may be generalized to cover cases in which the angular momentum is not zero and when, in addition to the potential of range a , there is also present a gradually decreasing potential which vanishes at infinity faster than r^{-2} .† The function G_n , describing the scattering, then satisfies

$$\frac{d^2 G_n}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} - U(r) - W(r) \right] G_n = 0 \quad (r < a), \quad (61)$$

$$\frac{d^2 G_n}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} - W(r) \right] G_n = 0 \quad (r > a). \quad (62)$$

The auxiliary functions \mathcal{G}_s must now satisfy the equation (61) for $0 \leq r \leq a$. As before, they vanish for $r = 0$, but, for $r = a$, the condition (51) is replaced by

$$\frac{d\mathcal{G}_s}{dr} = f\mathcal{G}_s, \quad (63)$$

where

$$f = \frac{1}{G_n^+} \frac{dG_n^+}{dr}, \quad (64)$$

G_n^+ being the solution of (62) which has the asymptotic form

$$G_n^+ \sim e^{i(kr - \frac{1}{2}n\pi)}. \quad (65)$$

Following an exactly similar procedure to that above, we find for the n th-order partial cross-section

$$\frac{\pi}{k^2} (2n+1) \left| \sum_s N_s \frac{w_s^2 e^{2i\eta_n}}{E_s - E - \frac{1}{2}i\Gamma_s} + 2e^{i\eta_n} \sin \eta_n \right|^2. \quad (66)$$

E_s , Γ_s , and N_s are again defined as in (59) and (56). η_n is the phase shift produced in the n th-order partial wave by a potential V where

$$\begin{aligned} \frac{8\pi^2m}{\hbar^2} V &= W \quad (r > a) \\ &\rightarrow \infty \quad (r = a). \end{aligned} \quad (67)$$

The second term thus represents the amplitude scattered by this potential.

w_s is no longer related to $\mathcal{G}_s(a)$ by the formula (59) but by the more general relation

$$\left\{ \frac{\hbar^2}{8\pi^2mi} (f - f^*) \right\}^{\frac{1}{2}} \mathcal{G}_s(a) = w_s. \quad (68)$$

With this definition, $\Gamma_s = |w_s|^2$, as before.

† For the extension to the case of a Coulomb field see Chap. III, § 5.1.

$$\text{If } W(r) = 0, \quad f - f^* = 4i[a\pi\{J_{-n-\frac{1}{2}}^2(ka) + J_{n+\frac{1}{2}}^2(ka)\}]^{-1}$$

and, if further, ka is small,

$$f - f^* = 2ik^{2n+1}(2a)^{2n} \left\{ \frac{n!}{(2n)!} \right\}^2,$$

giving
$$\Gamma_s = \frac{\hbar^2}{8\pi^2 ma} (2ka)^{2n+1} |\mathcal{G}_s(a)|^2 \left\{ \frac{n!}{(2n)!} \right\}^2. \quad (69)$$

It will be noted that, for the general case we have just discussed, there is a considerable ambiguity in choice of a . Different choices must lead, of course, to the same final result, but the relative importance of the dispersion and potential scattering terms can be varied greatly in this way. In most cases where the formula is useful the best choice of a is sufficiently clear to prevent serious ambiguity (see Chap. VIII, § 8.21).

III

SCATTERING OF A BEAM OF PARTICLES BY A COULOMB FIELD

1. Introduction

If a beam of charged particles, each carrying a charge $Z'\epsilon$, and such that one particle crosses unit area per unit time, falls on a single nucleus of infinite mass and charge $Z\epsilon$, then, according to Newtonian mechanics, the number of particles $I(\theta) d\omega$ scattered per unit time through an angle θ into the solid angle $d\omega$ is given by

$$I(\theta) = (ZZ'\epsilon^2/2mv^2)^2 \operatorname{cosec}^4 \frac{1}{2}\theta, \quad (1)$$

where m , v are the mass and velocity of the incident particles. This formula was first deduced by Rutherford; the proof is given in various text-books, and will not be reproduced here.† It is in agreement with experiment for the scattering of α -particles by heavy nuclei.

In this chapter we shall show that exactly the same formula may be deduced from the wave mechanics. We have therefore to consider the scattering of a stream of charged particles (electrons or α -particles) by a bare nucleus, the force between a particle and the nucleus varying as the inverse square of the distance. For $V(r)$, therefore, we have

$$V(r) = -Z\epsilon^2/r \quad (\text{electrons}),$$

and
$$V(r) = 2Z\epsilon^2/r \quad (\alpha\text{-particles}),$$

where Z is the atomic number of the scattering nucleus.

We shall write in general

$$V(r) = ZZ'\epsilon^2/r, \quad (2)$$

where $Z'\epsilon$ is the charge on the scattered particle, and Z' is to be taken positive or negative, according as the scattered particle is positively or negatively charged. The wave equation therefore is

$$\nabla^2\psi + \frac{8\pi^2m}{\hbar^2} \left(E - \frac{ZZ'\epsilon^2}{r} \right) \psi = 0. \quad (3)$$

We have to show that a solution can be obtained with the asymptotic form

$$\psi \sim I + Sf(\theta), \quad (4)$$

where I represents an incident wave, S the scattered wave, and

$$|f(\theta)| = (ZZ'\epsilon^2/2mv^2) \operatorname{cosec}^2 \frac{1}{2}\theta. \quad (5)$$

† Cf. Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances*, p. 191; or Andrade, *The Structure of the Atom*, p. 21.

We saw in Chapter II that the method given there for the calculation of the scattered amplitude is only applicable if $V(r)$ tends to zero faster than r^{-1} as r tends to infinity. This limitation arises from the fact that the bounded solution $L_n(r)$ of the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dL}{dr} \right) + \left[\frac{8\pi^2 m}{h^2} \left(E - \frac{ZZ'\epsilon^2}{r} \right) - \frac{n(n+1)}{r^2} \right] L = 0 \quad (6)$$

has asymptotic form†

$$(kr)^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n - \alpha \log 2kr) \quad (\alpha = 2\pi ZZ'\epsilon^2/hv), \quad (7)$$

which differs by the logarithmic term from the form assumed in Chap. II, eq. (15). Nevertheless, it has been shown by Gordon‡ that, corresponding to Chap. II, eq. (16), the wave function that describes the scattering is

$$\psi(r, \theta) = \sum_{n=0}^{\infty} (2n+1) i^n e^{i\eta_n} L_n(r) P_n(\cos \theta). \quad (8)$$

This function is shown by Gordon to be equal to§

$$e^{-i\pi\alpha} \Gamma(1+i\alpha) e^{ikr \cos \theta} {}_1F_1\{-i\alpha; 1; ikr(1-\cos \theta)\}, \quad (9)$$

and to have the asymptotic form

$$I + Sf(\theta),$$

with

$$I = \exp[ikz + i\alpha \log k(r-z)], \quad (10)$$

$$S = r^{-1} \exp[ikr - i\alpha \log kr], \quad (11)$$

and $|f(\theta)|$ given by (5). For the phase of $f(\theta)$, cf. eq. (16) of this chapter.

The forms (10), (11) for the incident and scattered waves are peculiar to the Coulomb field. They may be explained as follows.

If we consider all the classical hyperbolic orbits with one asymptote pointing from right to left parallel to the z -axis, we should expect the wave front of the incident wave to be normal to all these hyperbolae. At large distances from the nuclei the surface perpendicular to these hyperbolae does not tend to the form $z = \text{constant}$, but, as has been shown by Gordon,|| to the form

$$z + \frac{ZZ'\epsilon^2}{mv^2} \log k(r-z) = \text{const.}$$

The incident wave is, as it were, distorted even at infinity by the nucleus that it is going to encounter. Thus we should expect the incident wave to be

$$\exp \left[ik \left\{ z + \frac{ZZ'\epsilon^2}{mv^2} \log k(r-z) \right\} \right],$$

† This is proved in § 4, where η_n is found.

‡ Gordon, *Zeits. f. Physik*, 48 (1928), 180.

§ The function ${}_1F_1$ is defined in § 3 of this chapter.

|| Gordon, loc. cit.

which is the same as (10). The form of the scattered wave (11) may be explained in the same way.

In the following sections we shall show that (9) is a solution of the wave equation, and that it has the asymptotic form given by (10), (11), and (5). We shall not make use of the series (8) as in Gordon's method, but shall solve the wave equation directly. The method is one first given by Temple.†

2. Solution of the wave equation for scattering by a Coulomb field

The wave equation that we have to solve is

$$\nabla^2\psi + \left(k^2 - \frac{\beta}{r}\right)\psi = 0 \quad (\beta = 8\pi^2mZZ'\epsilon^2/\hbar^2). \quad (12)$$

We make the following substitution: we put

$$\psi = e^{ikz}F, \quad (13)$$

and obtain

$$\nabla^2F + 2ik\frac{\partial F}{\partial z} - \frac{\beta F}{r} = 0.$$

This partial differential equation possesses a solution of the type

$$F = F(r-z);$$

if we make this substitution we obtain

$$2\left(1 - \frac{z}{r}\right)F'' + \frac{2}{r}F' + 2ik\left(\frac{z}{r} - 1\right)F' - \frac{\beta}{r}F = 0,$$

F' , F'' being the first and second differential coefficients of F . If we multiply this equation by r , we see that r , z only occur in the form $r-z$, and therefore a solution exists of the required type. Putting

$$\zeta = r-z,$$

we obtain

$$\zeta\frac{d^2F}{d\zeta^2} + \frac{dF}{d\zeta} - ik\zeta\frac{dF}{d\zeta} - \frac{1}{2}\beta F = 0. \quad (14)$$

If we try for a solution

$$F = \zeta^\rho(1 + a_1\zeta + a_2\zeta^2 + \dots),$$

the indicial equation gives $\rho^2 = 0$, and the solution finite at the origin is therefore of the form

$$F = \sum_{n=0}^{\infty} a_n \zeta^n.$$

Substituting this into (14), and equating to zero the coefficient of ζ^n , we obtain the recurrence formula

$$[n(n+1) + (n+1)]a_{n+1} = a_n[ikn + \frac{1}{2}\beta],$$

† *Proc. Roy. Soc. A*, 121 (1928), 673.

and therefore
$$a_{n+1} = (ik)^{n+1} \prod_{s=0}^n \frac{(s + \frac{1}{2}\beta/ik)}{(s+1)^2}.$$

It follows that F is a hypergeometric function of the kind described in § 3; we have

$$F = {}_1F_1(-i\alpha; 1; ik\zeta),$$

where

$$\alpha = \frac{1}{2}\beta/k = 2\pi ZZ'\epsilon^2/hv.$$

The asymptotic expansion of F will be found in § 3; we see, from equation (24), that $F = W_1 + W_2$, where for large r

$$W_1 \sim (-ik\zeta)^{i\alpha} G_1 / \Gamma(1+i\alpha),$$

$$W_2 \sim (ik\zeta)^{-i\alpha-1} e^{ik\zeta} G_2 / \Gamma(-i\alpha),$$

where

$$G_1 = 1 + \frac{-\alpha^-}{ik\zeta} + \dots,$$

$$G_2 = 1 + (1+i\alpha)^2/ik\zeta + \dots$$

Taking the expansions as far as terms in ζ^{-1} , we have therefore

$$W_1 \sim \frac{e^{\frac{1}{2}\pi\alpha}}{\Gamma(1+i\alpha)} \left(1 - \frac{\alpha^2}{ik\zeta}\right) \exp(i\alpha \log k\zeta),$$

$$W_2 \sim \frac{-ie^{\frac{1}{2}\pi\alpha}}{\Gamma(-i\alpha)} \frac{e^{ik\zeta}}{k\zeta} \exp(-i\alpha \log k\zeta).$$

The functions W_1, W_2 , when multiplied by $\exp(ikz)$, represent the incident and scattered waves respectively. Since we require an incident wave of unit amplitude, we take for the total wave function representing the scattering†

$$\psi(r, \theta) = e^{-\frac{1}{2}\pi\alpha} \Gamma(1+i\alpha) e^{ikz} {}_1F_1(-i\alpha; 1; ik\zeta), \quad (15)$$

where $\alpha = 2\pi ZZ'\epsilon^2/hv$, $\zeta = r - z = r(1 - \cos \theta)$.

This wave function then has the asymptotic form

$$\psi \sim I + S f(\theta),$$

where

$$I = [1 - \alpha^2/ik(r-z)] \exp[ikz + i\alpha \log k(r-z)],$$

$$S = r^{-1} \exp[ikr - i\alpha \log kr],$$

$$f(\theta) = \frac{ZZ'\epsilon^2}{2m\upsilon^2} \operatorname{cosec}^2 \frac{1}{2}\theta \exp[-i\alpha \log(1 - \cos \theta) + i\pi + 2i\eta_0], \quad (16)$$

where

$$\exp 2i\eta_0 = \Gamma(1+i\alpha)/\Gamma(1-i\alpha).$$

† Sommerfeld, *Ann. d. Physik*, **11** (1931), 257, has given the following formula for this function,

$$\psi(r, \theta) = e^{-\frac{1}{2}\pi\alpha} e^{ikr} \int_0^\infty x^{i\alpha} e^{-x} J_0\{2\sqrt{(ik\zeta)x}\} dx,$$

where J_0 is the Bessel function defined in Whittaker and Watson, *Modern Analysis*, 4th edition, p. 355.

It is to be noted that Z' in these formulae is to be taken as $+2$ for α -particles, -1 for electrons.

The incident wave fronts and the scattered wave fronts have the forms (10) and (11).

The scattered intensity $I(\theta)$ is given by

$$I(\theta) = |f(\theta)|^2 = \left[\frac{ZZ'\epsilon^2}{2mv^2} \right]^2 \operatorname{cosec}^4 \frac{1}{2}\theta,$$

which is the Rutherford formula.

NOTE

At the origin (15) gives $|\psi|^2 = 2\pi\alpha/(e^{2\pi\alpha} - 1)$. (17)

For the case of a repulsive field, as between an α -particle and a nucleus, α is positive. If α is large and positive, e.g. for slow α -particles, $|\psi|^2$ is very small at the origin. This means that very few particles come near the nucleus.

If α is large and negative, e.g. for slow electrons, $|\psi|^2$ is fairly large at the origin, of order of magnitude $|\alpha|$.

If α is small, the solution (15) becomes at all points not very different from the plane wave $\exp(ikz)$.

That α should be small is also the condition of applicability of the Born approximation (Chap. VII), which consists in treating $V(r)$ as a perturbation. This may be seen by writing the wave equation in units of length $1/k$; we obtain

$$\nabla^2\psi + (1 - 2\alpha/r)\psi = 0.$$

3. The generalized hypergeometric series

We shall investigate in this section certain properties of the function used in § 2, defined by

$${}_1F_1(a; b; z) = 1 + \frac{a}{b \cdot 1}z + \frac{a(a+1)}{b(b+1) \cdot 1 \cdot 2}z^2 + \dots \quad (18)$$

Since we shall not have occasion to use any other function of hypergeometric type, we shall omit the suffixes. The function $M_{k,m}(z)$ defined by Whittaker† (confluent hypergeometric function) is connected with this function by the equation

$$M_{k,m} = z^{m+1/2} e^{-1/2z} {}_1F_1\left(\frac{1}{2} + m - k; 2m + 1; z\right).$$

It may be noted here that $F(a; b; z)$ is a solution of the differential equation

$$z \frac{d^2y}{dz^2} + (b-z) \frac{dy}{dz} - ay = 0, \quad (19)$$

as may easily be verified.

We require the asymptotic expansion of the function $F(a; b; z)$ for $|z|$ large, a and b remaining constant. This expansion is well known.

† Whittaker and Watson, *Modern Analysis*, 4th edition, p. 337.

We reproduce it here because of its importance in problems connected with Coulomb forces. The proof is similar to that given by Whittaker.†

We shall limit ourselves to the case when b is a positive integer, and z complex.

It is necessary for our purpose to express F as a contour integral. To do this we make use of the theorem that if m be any positive integer, then

$$\frac{1}{m!} = \frac{1}{2\pi i} \int_{\gamma} e^{t-m-1} dt, \quad (20)$$

where γ is any closed path encircling the origin once in an anti-clockwise direction. The proof is elementary.

Now F may be expressed in the following form:

$$F(a; b; z) = (b-1)! \sum_{n=0}^{\infty} c_n z^n / (b+n-1)!,$$

where c_n is the coefficient of x^n in the expansion of $(1-x)^{-a}$. Therefore, by means of (20), we have, putting $m = b+n-1$,

$$F(a; b; z) = \frac{(b-1)!}{2\pi i} \sum_{n=0}^{\infty} c_n z^n \int_{\gamma} e^{t-b-n} dt.$$

If we now choose our path γ so that on all points of it

$$|z/t| < 1, \quad (21)$$

then we may reverse the order of summation and integration, the series being convergent for all values of t . We obtain

$$F(a; b; z) = \frac{(b-1)!}{2\pi i} \int_{\gamma} \left(1 - \frac{z}{t}\right)^{-a} e^{t-b} dt. \quad (22)$$

It will be noticed that, by virtue of (21), the path of integration γ must encircle the point $t = z$. We can therefore, without altering the value of the integral, deform γ into any closed path which encircles the points $t = 0$ and $t = z$.

It is further clear that the integrand is a single-valued function of t , if a cut be made between the points $t = 0$ and $t = z$.

In order to find the asymptotic expansion of (22) we deform γ into the path γ' shown in Fig. 8. Owing to the factor e^t in the integrand, those parts of γ' for which the real part of t is large and negative contribute very little to the integral. If we make the parts of γ' marked AB , CD , in Fig. 8 tend to an infinite distance from the imaginary axis,

† Whittaker and Watson, *Modern Analysis*, 4th edition, p. 339.

then (22) may be replaced by the sum of the two integrals, one round the lower loop and the other round the upper. We set therefore

$$F(a; b; z) = W_1(a; b; z) + W_2(a; b; z), \tag{23}$$

where
$$W_1(a; b; z) = \frac{(b-1)!}{2\pi i} \int_{\gamma_1} \left(1 - \frac{z}{t}\right)^{-a} e^{t-b} dt$$

and γ_1 comes from $-\infty$, encircles the origin in an anti-clockwise direction, and returns to $-\infty$. W_2 is given by the same integrand, and a path that encircles the point $t = z$. Making in W_2 the substitution

$$t - z = u$$

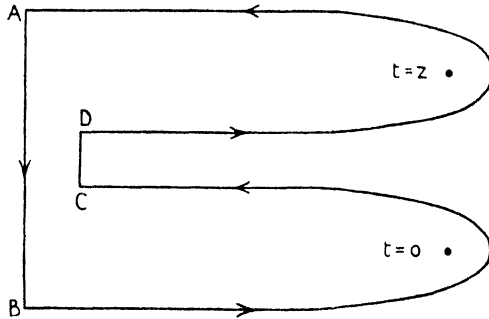


FIG. 8.

the path transforms into γ_1 encircling the origin; we obtain

$$W_2(a; b; z) = \frac{(b-1)!}{2\pi i} \int_{\gamma_1} u^{-a} e^{u+z} \frac{du}{(u+z)^{-a+b}}.$$

The asymptotic expansions of W_1 , W_2 may now be written down. We have

$$W_1 = \frac{(b-1)!}{2\pi i} (-z)^{-a} \int_{\gamma_1} \left(1 - \frac{t}{z}\right)^{-a} e^{t^{a-b}} dt,$$

$$W_2 = \frac{(b-1)!}{2\pi i} (+z)^{a-b} e^{z} \int_{\gamma_1} \left(1 + \frac{t}{z}\right)^{a-b} e^{t^{-a}} dt.$$

Expanding the brackets in the integrand, and making use of the theorem that†

$$\frac{1}{\Gamma(x)} = \frac{1}{2\pi i} \int_{\gamma_1} e^{t^{-x}} dt,$$

† Ibid., pp. 244-5.

we obtain

$$\left. \begin{aligned} W_1 &\sim \frac{\Gamma(b)}{\Gamma(b-a)} (-z)^{-a} G(a, a-b+1; -z) \\ W_2 &\sim \frac{\Gamma(b)}{\Gamma(a)} e^{xz} z^{a-b} G(1-a, b-a; z), \end{aligned} \right\} \quad (24)$$

where G denotes the semi-convergent series

$$G(\alpha, \beta; z) = 1 + \frac{\alpha\beta}{z \cdot 1!} + \frac{\alpha(\alpha+1)\beta(\beta+1)}{z^2 \cdot 2!} + \dots$$

From (23) we obtain the asymptotic expansion of F .

4. The radial wave functions for positive energy states in a Coulomb field

We consider now the solutions of the equation (6). Although it is possible to calculate the scattering by a pure Coulomb field without use of these solutions, as in § 2, they are required for the discussion of any scattering problem in which a deviation from the Coulomb field occurs. Thus they are of importance in nuclear problems (see § 5 and Chap. XIII, §§ 1.2, 2.35).

Writing $k^2 = 2mE/\hbar^2$, $\alpha = ZZ'\epsilon^2/\hbar v$, $\rho = kr$, the equation (6) takes the form

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{dL}{d\rho} \right) + \left\{ 1 - \frac{2\alpha}{\rho} - \frac{n(n+1)}{\rho^2} \right\} L = 0. \quad (25)$$

The substitution $L = \rho^n e^{i\rho} F$ leads to the equation

$$\rho \frac{d^2 F}{d\rho^2} + 2(n+1+i\rho) \frac{dF}{d\rho} + 2\{(n+1)i-\alpha\} F = 0,$$

which, by the further substitution

$$\rho = \frac{1}{2} iz,$$

$$\text{gives} \quad z \frac{d^2 F}{dz^2} + (2n+2-z) \frac{dF}{dz} - (i\alpha+n+1) F = 0, \quad (26)$$

which is of the form (19).

Two independent solutions of this equation are thus

$$W_{1,2}(i\alpha+n+1, 2n+2, z).$$

4.1. The bounded solution, L_n

The solution which is regular at the origin will be

$$F(i\alpha+n+1, 2n+2, z) = W_1 + W_2. \quad (27)$$

The asymptotic expansion may be found from (24). If we take for the bounded solution of (6)

$$L_n = e^{-i\pi\alpha} \frac{|\Gamma(n+1+i\alpha)|}{(2n+1)!} (2kr)^n e^{ikr} F(i\alpha+n+1; 2n+2; -2ikr), \quad (28)$$

then $L_n \sim (kr)^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n - \alpha \log 2kr)$

with $\eta_n = \arg \Gamma(n+1+i\alpha)$.

4.2. *The unbounded solution, K_n*

It is convenient to choose as second solution K_n , that one which has the asymptotic form

$$K_n \sim (kr)^{-1} \cos(kr - \frac{1}{2}n\pi + \eta_n - \alpha \log 2kr), \quad (29)$$

so that $K_n = ie^{-i\pi\alpha} \frac{|\Gamma(n+1+i\alpha)|}{(2n+1)!} (2kr)^n e^{ikr} [W_1 - W_2]$. (30)

The series expansion of K_0 has been discussed by Sexl† and extended to any value of n by Yost, Wheeler, and Breit.‡ They find that

$$K_n = \frac{1}{\pi} (e^{2\pi\alpha} - 1) \times \left\{ \log 2kr + 2\gamma - \sum_1^{2n+1} s^{-1} + \sum_1^n \frac{s}{s^2 + \alpha^2} + \text{R.P.} \frac{\Gamma'(i\alpha)}{\Gamma(i\alpha)} \right\} L_n + H_n, \quad (31)$$

where

$$H_n = 2e^{i\pi\alpha} \text{R.P.} e^{i(kr-\eta_n)} \left\{ \sum_{s=0}^{2n} \frac{(-i)^s (2n-s)!}{s! \Gamma(n-s+1-i\alpha)} (2kr)^{s-n-1} - \frac{1}{\pi} \sinh \pi\alpha \sum_{s=1}^{\infty} (-i)^s \frac{\Gamma(n+1+s+i\alpha)}{(2n+1+s)! s!} (2kr)^{s+n} a_{ns} \right\},$$

and $a_{ns} = \sum_{t=1}^s \left(\frac{1}{t} + \frac{1}{2n+1+t} - \frac{1}{n+t+i\alpha} \right)$.

In these expressions R.P. denotes the ‘real part of’ and γ is Euler’s constant.

4.3. *Numerical calculation of L_n and K_n*

The forms (28) and (31) are not convenient for calculation as they involve imaginary numbers. Yost, Wheeler, and Breit§ have obtained series expansions, involving real numbers only, which are convenient to use provided ρ is not too large. They also discussed methods which are available when the series expansions converge too slowly. Tables of the

† *Zeits. f. Physik*, 56 (1929), 72; 81 (1933), 163.

‡ *Phys. Rev.* 49 (1936), 174.

§ *Ibid.*

functions for repulsive fields have been constructed for $n = 0, 1, 2$ and a wide range of values of α and kr .†

5. The penetrability of a Coulomb potential barrier

A particle of charge $Z\epsilon$ approaching an atomic nucleus of charge $Z'\epsilon$ is repelled by the Coulomb potential $ZZ'\epsilon^2/r$ at distances r greater than the nuclear radius R . The problem we now consider is the determination of the chance that a particle of given initial kinetic energy ($< ZZ'\epsilon^2/R$) and angular momentum will penetrate to a distance R in spite of the repulsion. Let $r^{-1}G_n$ be the proper radial wave function for the motion, in the modified Coulomb field, of a particle of given angular momentum $\{n(n+1)\}^{\frac{1}{2}}\hbar$, which has the asymptotic form

$$G_n \sim \sin(kr - \frac{1}{2}n\pi - \alpha \log 2kr + \eta_n + \sigma_n), \quad (32)$$

where σ_n is the additional phase shift due to the departure from the Coulomb field for $r < R$. We may then define $G_n^2(R)$ as the penetrability $\exp(-P_n)$ for this case.

The most convenient method of estimating P_n is to use Jeffreys's method of approximation, as in Chap. I, § 6. The equation for G_n may be written

$$\frac{d^2 G_n}{dr^2} + f(r)G_n = 0,$$

$$\text{where} \quad f(r) = k^2 - \frac{8\pi^2 m ZZ'\epsilon^2}{\hbar^2 r} - \frac{n(n+1)}{r^2} \quad (r > R). \quad (33)$$

At the classical closest distance of approach R_0 , $f(R_0) = 0$. For $r > R_0$ the solution is oscillatory. For $r < R_0$ an exponentially increasing or decreasing solution may be found. We require that solution which decreases as r decreases below R_0 . According to Jeffreys's approximation this solution is

$$\begin{aligned} G_n &= \left[\frac{-f(r)}{k^2} \right]^{-\frac{1}{4}} \exp \left\{ \int_{R_0}^r [-f(r)]^{\frac{1}{2}} dr \right\} \quad (r < R_0), \\ &= \left[\frac{f(r)}{k^2} \right]^{-\frac{1}{4}} \sin \left\{ \frac{1}{4}\pi + \int_{R_0}^r [f(r)]^{\frac{1}{2}} dr \right\} \quad (r > R_0). \end{aligned} \quad (34)$$

From this we have, for the penetration probability

$$e^{-P_n} = [-k^2/f(R)]^{\frac{1}{2}} \exp \left\{ 2 \int_{R_0}^R [-f(r)]^{\frac{1}{2}} dr \right\}. \quad (35)$$

Two distinct approximations are really involved in (35). The effect

† Yost, Wheeler, and Breit, loc. cit.; *ibid. Terr. Mag. and Atmos. Elec. Dec.* (1935), 443; Wicker, *ibid.*, Dec. (1936), 390.

of the interaction for $r < R$ on the wave function L_n is ignored so that it is taken to be the function (28) for an unmodified Coulomb field. This is likely to be a good approximation if the penetration is small. However, the further approximation is made of representing the function (28) by Jeffreys's approximation. The accuracy of this has been investigated by Yost, Wheeler, and Breit.† They find that, while (35) is, in this respect, a fair approximation, the accuracy is much improved by replacing $n(n+1)$ in $f(r)$ by $(n+\frac{1}{2})^2$.‡

Substituting for $f(r)$ from (33) we find, on integrating

$$P_n = -2\beta(y+1-x)^{\frac{1}{2}} + \alpha \left\{ \pi + 2 \arcsin \frac{1-2x}{(1+4xy)^{\frac{1}{2}}} \right\} + 2\{n(n+1)\}^{\frac{1}{2}} \log \left\{ \frac{1+2y+2y^{\frac{1}{2}}(y+1-x)^{\frac{1}{2}}}{(1+4xy)^{\frac{1}{2}}} \right\} - \frac{1}{2} \log \frac{x}{1+y-x}, \quad (36)$$

where $\beta = (8\pi^2 m Z Z' \epsilon^2 R / h^2)^{\frac{1}{2}}$, $x = k^2 R^2 / \beta^2$, and $y = n(n+1) / \beta^2$ are the respective ratios of the initial kinetic energy and of the rotational energy to the barrier height at the nuclear radius. It is only necessary to substitute $(n+\frac{1}{2})^2$ for $n(n+1)$ throughout this formula if the improved approximation is to be employed.

5.1. The dispersion formula with a Coulomb field

In deriving the dispersion formula (64) Chap. II for the scattering cross-section it was assumed that, in addition to the potential of range a , there was also present a gradually decreasing potential which vanished at infinity faster than r^{-2} . If, instead, the additional potential is of the Coulomb form, $Z Z' \epsilon^2 / r$, so that, for $r > a$, the function G_n of (62) Chap. II satisfies

$$\frac{d^2 G_n}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} - \frac{8\pi^2 m}{h^2} \frac{Z Z' \epsilon^2}{r} \right] G_n = 0, \quad (37)$$

we may define the quantity f in the same way as in (63) and (64) of Chapter II but with G_n^+ chosen to be that solution of (37) which has the asymptotic form

$$G_n^+ \sim \exp\{i(kr - \frac{1}{2}n\pi - \alpha \log 2kr)\}, \quad (38)$$

where α has the same significance as in § 4. The formula (66) of Chapter II is then regained, but with η_n now defined so that the asymptotic form of the proper solution of the equation for motion with angular momentum $\{n(n+1)\}^{\frac{1}{2}}\hbar$ in a field of potential

$$\begin{aligned} V &= Z Z' \epsilon^2 / r \quad (r > a) \\ &\rightarrow \infty \quad (r = a), \end{aligned} \quad (39)$$

is $\sin(kr - \frac{1}{2}n\pi - \alpha \log 2kr + \eta_n)$.

We find now that, at $r = a$,

$$f - f^* = \frac{2i}{ka^2} \{K_n^2(a) + L_n^2(a)\}^{-1},$$

† *Phys. Rev.* **49** (1936), 174.

‡ See Chap. VII, § 6.2.

where L_n, K_n have the same significance as in §§ 4.1, 4.2 respectively. This gives, following Chap. II (68),

$$\Gamma_s = \frac{\hbar^2}{ma} \frac{1}{ka} \frac{|\mathcal{G}_s(a)|^2}{K_n^2(a) + L_n^2(a)}. \quad (40)$$

We may use Jeffreys's approximation for the functions K_n, L_n . If at $r = a$ the Coulomb repulsive energy is greater than the initial kinetic energy, this gives

$$\left. \begin{array}{l} K_n \\ L_n \end{array} \right\} = [-k^2 f(a)]^{-\frac{1}{2}} \exp \pm \int_{R_0}^a [-f(r)]^{\frac{1}{2}} dr,$$

where $f(r)$ and R_0 are as in (33). We find then, if the penetration is small,

$$\Gamma_s = \frac{k\hbar^2}{m} e^{-P_n} |\mathcal{G}_s(a)|^2$$

where P_n is defined as in (35).

Comparison with the formula (69) of Chapter II for the case $n = 0$ shows that the effect of the Coulomb field is merely to introduce the penetration factor, as would be expected.

IV

THE SPIN OF THE ELECTRON

1. The magnetic moment of an atom

FOR some collision problems it is necessary to take account of the spin of the electron. We must therefore give a treatment of the spin suitable for use in such problems.

The hypothesis that an electron has an axis of symmetry, and thus a fourth degree of freedom, was introduced in 1925 before the discovery of the new quantum mechanics, in order to account for the four quantum numbers that were found to be necessary for the classification of atomic energy levels. In the new quantum theory, methods for treating the spin were developed by Pauli[†] and Darwin.[‡] Finally, Dirac,[§] by means of a proper relativistic treatment of the wave equation, was able to show that the spin was a necessary consequence of the principle of relativity. In this chapter a treatment of the spin will first be given, which is equivalent to that of Pauli, and which is sufficient for all cases in which the spin influences the symmetry of the wave functions, but the interaction of the spin forces with the atomic fields can be neglected. This is the case in all collision problems where the velocity of the electrons considered is small compared with that of light. We shall also show the connexion between this treatment and the treatment based on Dirac's equation, and shall discuss a collision problem in which the spin forces cannot be neglected.

In Dirac's relativistic treatment of the spin the properties of the electron can be deduced from quite general assumptions. In the more elementary treatment, however, one takes the properties of the spin deduced from experiment, and describes them in the notation of wave mechanics. We begin with the fact, proved by the experiments of Gerlach and Stern, that an atom with one electron in an S state in the outer ring has a magnetic moment equal to $e\hbar/4\pi mc$ (one Bohr magneton). For convenience, we shall refer to such an atom as a hydrogen atom.

We must first remark that if we are given a hydrogen atom of which the direction of the magnetic moment is not known, it is impossible

[†] Pauli, *Zeits. f. Physik*, **43** (1927), 601.

[‡] Darwin, *Proc. Roy. Soc. A*, **116** (1927), 227; see also Dirac, *Quantum Mechanics*, 3rd edition, p. 149.

[§] Dirac, *Proc. Roy. Soc. A*, **117** (1928), 610; also *Quantum Mechanics*, 3rd edition, Chap. XI.

by any conceivable experiment to discover this direction. This can be shown by the following argument. Suppose that an attempt were made to measure the field H outside an atom, in order to discover the direction of the magnetic moment. This might be done by shooting an electron past the atom and observing its deflexion. We can find the order of magnitude of this deflexion as follows: If the electron passes the atom at a distance r , the order of magnitude of H at points where the electron passes will be

$$H \sim M/r^3 \quad (M = \epsilon h/4\pi mc).$$

The force on the electron is $\epsilon H v/c$. This force acts on the electron for a time of order of magnitude r/v , and produces, therefore, a momentum of order of magnitude $\epsilon H r/c$. The deflexion produced is thus $\epsilon H r/mc v$. This deflexion, to be observable, must be greater than the natural spreading of the beam of waves that represents the electron. If Δr is the breadth of this beam, then the spreading will be $h/mv\Delta r$. Thus we must have

$$\epsilon H r/mc v > h/mv\Delta r.$$

Putting in the value of H , we obtain

$$\Delta r/r > r/r_e \quad (r_e = \epsilon^2/mc^2 \sim 2.8 \times 10^{-13} \text{ cm}).$$

Now r must be greater than the radius of the atom if the effect is to be observable. Thus we see that Δr is at least 20,000 times greater than r . The observation is therefore impossible.

We can determine the moment of a single atom only by means of a Stern-Gerlach experiment, and this experiment does not leave the atom undisturbed. The Stern-Gerlach experiment proves that a hydrogen atom in a magnetic field H must acquire additional energy equal either to $\pm MH$; the experiment, further, can separate the atoms having the two different energies. Since we have seen that the direction of the magnetic moment cannot be measured, *we must define the statement that the magnetic moment of an atom points in the direction \mathbf{l} , where \mathbf{l} is a unit vector, as meaning that the atom has been passed through an inhomogeneous magnetic field H in the direction \mathbf{l} , and that the atom was in the deflected beam having energy $-HM$.*

We must now ask in what respect an atom that has been prepared in this way is different from any other atom. We wish to know whether any predictions can be made about its future behaviour that could not be made about an atom that had not been so prepared. We have seen that the direction of its magnetic moment cannot be measured. We can, however, put it through a second inhomogeneous magnetic field H' in a new direction \mathbf{l}' , and observe whether the atom takes up energy

$\pm H'M$ in this new field. From our knowledge of the way in which the atom has been prepared, it is possible to predict the probability that the atom will take up either of these energies.† In the special case where \mathbf{l} and \mathbf{l}' refer to the same direction it is of course certain that the energy will be $-H'M$. We shall now see how to calculate the probability in the more general case. To do this we must express our results in the notation of quantum mechanics.

We describe our knowledge of an atom whose magnetic moment has been orientated in the direction \mathbf{l} by a Stern-Gerlach experiment, by a wave function

$$\chi_l(s).$$

The argument s of the wave function must refer to what is observable about the atom, namely, the energy that the atom would take up if passed into a second inhomogeneous magnetic field. We take therefore an arbitrary direction in space—say the z -axis—and denote by $H'M_s$ the energy that the atom would have if passed into a magnetic field H' in this direction. Then the probability that this energy will have a given value is $|\chi(s)|^2$; we know that χ must be zero unless s is ± 1 . χ therefore has only two non-zero values, $\chi(+1)$ and $\chi(-1)$; the squares of the moduli of these give the probabilities that the energy shall have the values $\pm MH'$. It is clear that $|\chi_l(s)|^2$ will depend only on the angle between \mathbf{l} and the z -axis.

If \mathbf{l} lies along the z -axis, so that the energy is $-MH$, we have for χ

$$\left. \begin{aligned} \chi(+1) &= 0 \\ \chi(-1) &= 1 \end{aligned} \right\} \quad (1)$$

Let us denote this function by $\chi_\beta(s)$. Similarly let χ_α be the corresponding function when \mathbf{l} lies in the opposite direction, namely,

$$\left. \begin{aligned} \chi_\alpha(+1) &= 1 \\ \chi_\alpha(-1) &= 0 \end{aligned} \right\} \quad (2)$$

We note that χ_α , χ_β defined in this way are both normalized and are orthogonal to each other.

The two wave functions χ_α and χ_β describe the two *stationary states* of the system—i.e. the two states in which the energy is known. The general state of the system will be described by a wave function

$$A\chi_\alpha + B\chi_\beta,$$

† Unless the field changes so abruptly that the atom passes from H to H' in a time small compared to the period of Larmor precession, no splitting will occur in the second experiment. The exact condition has been investigated by Rosen and Zener, *Phys. Rev.* **40** (1932), 502.

where A and B are arbitrary complex constants satisfying the normalizing condition,

$$AA^* + BB^* = 1.$$

It can be shown† by arguments depending on invariance with respect to change of axes that if the atom is prepared with its magnetic moment lying in a direction specified by spherical polar angles θ , ϕ , and if also s refers to energies in a magnetic field along the z -axis ($\theta = 0$), then we have

$$B/A = -\cot \frac{1}{2}\theta e^{i\phi}, \quad (3)$$

and thus, neglecting an arbitrary phase,

$$A = -\sin \frac{1}{2}\theta, \quad B = \cos \frac{1}{2}\theta e^{i\phi}.$$

The probability, therefore, that the atom will take up energy $-MH$ in the new field is $\cos^2 \frac{1}{2}\theta$, and that it will take up energy $+MH$ is $\sin^2 \frac{1}{2}\theta$.

The probability that the electron is at a given distance r from the nucleus will be approximately the same as it would be if the atom were not in a magnetic field, and will therefore be given by the square of the Schrödinger wave function

$$\psi(r) = (\pi a_0^3)^{-\frac{1}{2}} e^{-r/a_0}.$$

The complete wave function of the atom will therefore be the product

$$\psi(r)\chi(s).$$

This wave function will, however, be only approximately correct, because the charge distribution in an atom may well depend slightly on the orientation of the spin in a magnetic field.

We can, however (more accurately), describe the atom by a wave function

$$\psi(\mathbf{r}, s) \quad (s = 1, -1). \quad (4)$$

The interpretation of this wave function is as follows: the function

$$|\psi(\mathbf{r}, s)|^2 dx dy dz \quad (s = 1)$$

is the probability that the atom would have energy $+MH$ in a magnetic field along the z -axis, and that the electron would be found in a volume element $dx dy dz$.

The form of the function $\psi(\mathbf{r}, s)$ can only be found by applying the relativistic theory of the electron due to Dirac. It will be noticed that it is immaterial whether we write the wave function in the form (4), or whether we write *two* separate functions of \mathbf{r} , $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$. For velocities of the electron much less than c , both ψ_a and ψ_b are approximately solutions of Schrödinger's equation.

† Dirac, *Quantum Mechanics*, 1st edition, p. 132.

2. Magnetic moment of the electron

We have discussed so far only the magnetic moment of the atom. We shall not review here the evidence, derived from the anomalous Zeeman effect, from the gyromagnetic effect, etc., that the *electron* has a fourth degree of freedom, a magnetic moment $\epsilon\hbar/4\pi mc$, and a mechanical moment $\frac{1}{2}\hbar/2\pi$. We shall content ourselves with remarking that according to the Schrödinger theory the ground state of the hydrogen atom is not degenerate, and therefore, in order to account for the splitting in a magnetic field revealed by the Stern-Gerlach experiment, it is necessary to assume that the electron has a fourth degree of freedom.

The present evidence that electrons have a magnetic moment is derived from their behaviour when bound in stationary states in atoms. For the study of collision problems it is necessary to inquire what meaning can be attached to the magnetic moment of a free electron. In the first place, just as in the case of the atom, it is impossible to determine the moment by means of a magnetometer experiment. This can be shown by the following argument, due to Bohr.† Let us suppose that the position of the electron is known with an accuracy Δr and that we wish to determine the magnetic moment at a point distant r from it. It will not be possible to deduce from our measurement anything about the magnetic moment of the electron unless

$$\Delta r \ll r. \quad (5)$$

The field H that we wish to observe will be of order of magnitude

$$H \sim M/r^3.$$

If, however, the electron is in motion with velocity v , there will be a magnetic field due to its motion, of amount $\epsilon v/cr^2$; since we do not know v exactly we cannot allow for this field exactly. From our measurements, therefore, of the magnetic field, it will not be possible to find out anything about the magnetic moment of the electron, unless

$$M/r^3 \gg \epsilon\Delta v/cr^2,$$

where Δv is the uncertainty in our knowledge of v . Since by the uncertainty principle $\Delta r\Delta v > h/m$, this leads to

$$\Delta r \gg r,$$

which contradicts the inequality (5). We conclude therefore that it is not possible to measure the magnetic moment of an electron in this manner.

We shall now show that it is impossible, by means of a Stern-Gerlach

† Cf. Mott, *Proc. Roy. Soc. A*, 124 (1929), 440.

experiment, to determine the magnetic moment of a free electron, or to prepare a beam of electrons with the magnetic moments all pointing in the same direction. The argument is also due to Bohr.

In Fig. 9 a beam of electrons is supposed to travel parallel to the z -axis (i.e. perpendicular to the plane of the paper). The pole pieces of the magnet are shown, as are also the lines of force. The purpose of the

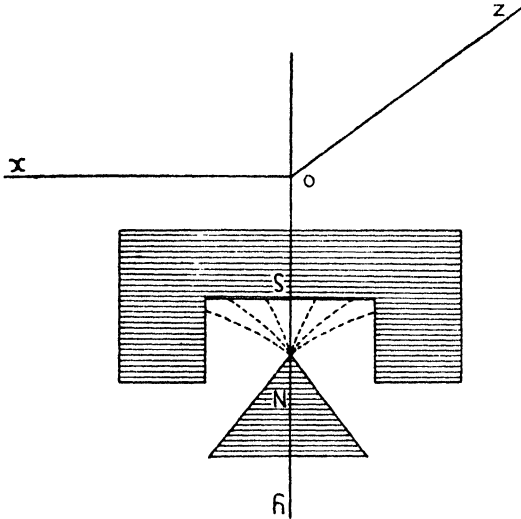


FIG. 9.

experiment is to observe a splitting in the y -direction. The force on an electron tending to split the beam will be

$$\pm M \frac{\partial H_y}{\partial y}. \quad (6)$$

Now all electrons will experience a force due to their motion through the field. Those moving in the plane Oyz will experience a force in the direction Ox . This force is perpendicular to the direction of the splitting, and its only effect will be to displace the beams to the right or to the left. However, electrons which do not move in the plane Oyz will experience a force in the direction Oy , because the lines of force in an inhomogeneous magnetic field cannot be straight, and there must be a component H_x of H along Ox . This force will have magnitude

$$\epsilon v H_x / c. \quad (7)$$

We can compare (7) with the force (6) tending to produce the splitting.

H_x at a point distant Δx from the plane Oyz will be equal to $\frac{\partial H_x}{\partial x} \Delta x$,

and since $\text{div } H$ vanishes, this is equal to $-\frac{\partial H_y}{\partial y} \Delta x$. The quantities (6) and (7) therefore stand in the ratio

$$\frac{\epsilon h}{4\pi mc} \frac{\partial H_y}{\partial y} : \frac{\epsilon v}{c} \frac{\partial H_y}{\partial y} \Delta x.$$

Dividing through by common factors this becomes

$$1 : 4\pi\Delta x/\lambda, \quad (7.1)$$

where λ is the wave-length h/mv of the waves that represent the electrons. Suppose now that $\pm\Delta x$ is the distance from the plane Oyz of the two extremities of the beam. Since Δx must be greater than λ , it is clear that the two extremities of the beam will be deflected in opposite directions through angles greater than the angle of splitting, which we hope to observe.

To see now that it is impossible to observe any splitting, let us consider the trace that the beam would make on a photographic plate. Suppose that it were possible to use finer beams than is allowed by the uncertainty principle, so that the thickness Δy of the beam in the y -direction would be infinitely small. Before passing through the magnetic field, the cross-section of the beam would be as in Fig. 10(a). Afterwards, it would be as in Fig. 10(b), which shows the trace produced on a photographic plate. The tilting of the traces is produced by the Lorentz forces discussed above. If ABC , $A'B'$ are two lines parallel to Oy and distant λ apart, then by (7.1) we see that the tilting is so great that $AB > BC$. If $A\beta\gamma$ is drawn perpendicular to the traces, it follows that $A\beta > \beta\gamma$. But $A\beta < \lambda$, and hence $\beta\gamma$, the distance between the traces, is less than λ . Thus the maximum separation that can be produced is λ . But actually we cannot obtain a trace of breadth comparable with λ . Therefore it is impossible to observe any splitting.

From these arguments we must conclude that it is meaningless to assign to the free electron a magnetic moment. It is a property of the electron that when it is bound in an S state in an atom, the atom has a magnetic moment. When we consider the relativistic treatment of the electron due to Dirac, we shall see that this magnetic moment is not in general equal to $\epsilon h/4\pi mc$, unless the velocities of the electron within the atom are small compared with that of light (§ 3.3). A single electron bound in its lowest state in the field of a nucleus of charge $Z\epsilon$ gives, according to Dirac's theory, a magnetic moment†

$$\frac{1}{2}[1 + 2\sqrt{(1-\gamma^2)}]\epsilon h/4\pi mc \quad (\gamma = 2\pi Z\epsilon^2/hc). \quad (8)$$

† This formula is due to Breit, *Nature*, **122** (1928), 649. Cf. § 3.3 of this chapter.

The statement that a free electron has four degrees of freedom is on a different footing, for it is hardly conceivable that an electron in an atom should have four degrees of freedom, and a free electron three. It is interesting to inquire, therefore, whether there is any conceivable experiment by which this fourth degree of freedom could be detected.

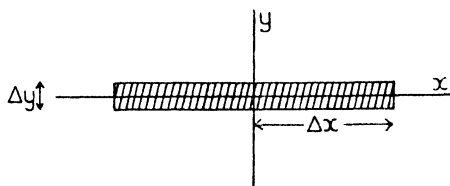


FIG. 10(a).

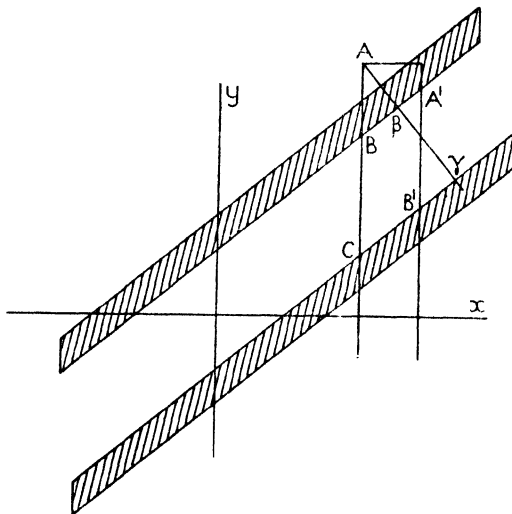


FIG. 10(b).

We wish to know whether it is possible to prepare a beam of electrons that is in some sense 'polarized', and whether it would be possible to detect this polarization.

There is at present no certain experimental evidence on this point; theoretical considerations show, however, that it is possible, in principle, both to prepare a polarized beam and to detect the polarization. Let us consider the following experiment.† A beam of atoms is prepared, by means of a Stern-Gerlach experiment, with their axes all pointing in the same direction, say along the z -axis. Electrons are ejected from

† This method of preparing a polarized beam of electrons was first suggested by Fues and Hellmann, *Phys. Zeits.* 31 (1930), 465.

these atoms by illuminating them with ultra-violet light. The beam of electrons obtained may be said to be polarized, for the following reasons: Assuming for the moment that the electron behaves like a small magnet, let us ask whether forces sufficient to eject the electron would be sufficient to alter appreciably the direction of the magnetic moment. The following purely classical considerations of the order of magnitude of the forces involved show that they are not, and so we may consider that the magnetic moments in the beam of ejected electrons all point in the same direction.†

If an electric field of intensity E acts on an electron for time t , the kinetic energy acquired is $\frac{1}{2}(Ee)^2t^2/m$. The energy that must be given to an electron to remove it from an atom is of order of magnitude $m\epsilon^4/h^2$. Thus to remove an electron from an atom the product of E and t must be of order of magnitude $Et \sim \epsilon m/h$. The average velocity of an electron in an atom is ϵ^2/h . The average couple acting on the electron magnet, due to its motion through the electric field E , will be of order

$$E \frac{\epsilon h}{mc} \frac{\epsilon^2}{h} \frac{1}{c},$$

which is equal to $E\epsilon^3/mc^2$. To change the orientation of the electron by an angle comparable with π , this couple must produce a change of angular momentum comparable with h . The time T necessary for this to occur is given by

$$T \frac{E\epsilon^3}{mc^2} \sim h,$$

which gives

$$ET \sim hmc^2/\epsilon^3.$$

We deduce that

$$\frac{ET}{Et} \sim \left(\frac{hc}{\epsilon^2}\right)^2.$$

Thus

$$T \gg t.$$

It would, however, be meaningless to speak of a polarized beam, unless the fact that the beam is polarized could be detected in some way. This could be done if the beam were passed through a gas of ionized atoms, so that some of the electrons were captured. If the neutral atoms formed were shown by means of a Stern-Gerlach experiment to be polarized, then we should have a method of detecting the polarization. The argument used above about the order of magnitude

† There is, of course, a small probability that the direction of the spin-axis is reversed, and the following discussions show this to be of order of magnitude $(1/137)^2$. There is no known method by means of which a completely polarized beam can be produced.

of the forces involved indicates that this should be the case; a proper proof can, however, be given on the basis of Dirac's theory of the electron.

Another less direct but possibly more practical method of preparing and of detecting a polarized beam is discussed in § 4.1.

We see, then, that the spin of a free electron may be described by the same wave function $\chi_i(s)$ that was used before to describe the magnetic moment of an atom. The function

$$|\chi_i(s)|^2 \quad (s = \pm 1)$$

gives the probability that, if the electron is prepared with its magnetic moment in the direction \mathbf{l} , then, if the electron be captured by an atom, and if that atom be passed into an inhomogeneous magnetic field, the energy of that atom will be either $\pm MH$. It is necessary to give to the square of the amplitude of the wave function this rather complicated interpretation, because it is not possible to measure the energy of an electron in a magnetic field, unless the electron is captured in an atom. It is further to be noted that, by the statement that an electron is prepared with its magnetic moment in a given direction, it is meant that the electron has been knocked off an atom that has been so prepared.

As in the case of the bound electron, an electron is completely described by a wave function

$$\psi(\mathbf{r}, s).$$

If the forces acting on the electron are so small that the direction of the spin remains constant throughout the experiment considered, then as before this function may be split up into the product

$$\psi(\mathbf{r})\chi(s),$$

when $\psi(\mathbf{r})$ is a solution of Schrödinger's equation. The form of $\psi(\mathbf{r}, s)$ when this is not the case can be found from Dirac's theory.

3. The relativistic wave equation

As is well known, Dirac has been able to show that it is impossible to find a wave equation for an electron that is invariant with respect to a Lorentz transformation, and which is linear in the time differential, unless the electron be assumed to have a fourth degree of freedom. If one assumes this, it can be deduced that a hydrogen atom has a magnetic moment of the observed magnitude, without any further special assumptions. An understanding of the elements of Dirac's theory is

essential to the further development of our subject, and we shall therefore give an outline of it here.

According to this theory the electron is described by *four* wave functions

$$\psi_\lambda(x, y, z, t) \quad (\lambda = 1, 2, 3, 4).$$

The probability that an electron will be in a volume-element $d\tau$ at time t is

$$\sum_{\lambda=1}^4 |\psi_\lambda|^2 d\tau. \quad (9)$$

The four functions ψ_λ satisfy the simultaneous differential equations†

$$\begin{aligned} (p_0 + mc)\psi_1 + (p_1 - ip_2)\psi_4 + p_3\psi_3 &= 0 \\ (p_0 + mc)\psi_2 + (p_1 + ip_2)\psi_3 - p_3\psi_4 &= 0 \\ (p_0 - mc)\psi_3 + (p_1 - ip_2)\psi_2 + p_3\psi_1 &= 0 \\ (p_0 - mc)\psi_4 + (p_1 + ip_2)\psi_1 - p_3\psi_2 &= 0, \end{aligned} \quad (10)$$

where

$$\begin{aligned} p_0 &= -\frac{h}{2\pi i} \frac{1}{c} \frac{\partial}{\partial t} + \frac{\epsilon V}{c}, \\ p_1 &= \frac{h}{2\pi i} \frac{\partial}{\partial x} + \frac{\epsilon A_1}{c}, \text{ etc.} \end{aligned}$$

V and \mathbf{A} are scalar and vector potentials. We have to show that these equations describe an electron having the properties outlined in the preceding section.

We first note that if we wish to find a periodic solution, p_0 must be replaced by $(W + \epsilon V)/c$, W being the energy of the electron. Secondly, if we assume that the velocity of the electron is small compared with that of light, so that

$$W - mc^2 \ll W + mc^2,$$

then it is easy to see that ψ_3, ψ_4 both satisfy Schrödinger's equation. Further, if ψ is any solution of Schrödinger's equation, an approximate solution of (10) is

$$\begin{aligned} \psi_3 &= A\psi \\ \psi_4 &= B\psi \\ \psi_1 &= -\{B(p_1 - ip_2) + Ap_3\}\psi/2mc \\ \psi_2 &= -\{A(p_1 + ip_2) - Bp_3\}\psi/2mc. \end{aligned} \quad (11)$$

A and B are arbitrary constants, and p_1, p_2, p_3 are to be interpreted as operators. It is clear that ψ_1, ψ_2 are much smaller than ψ_3, ψ_4 and can be neglected in the expression (9) for the charge density. Thus, if

† Darwin, *Proc. Roy. Soc. A*, 118 (1928), 654.

(9) is normalized to unity, and if we wish our four functions to be normalized also, we must have to this approximation

$$AA^* + BB^* = 1.$$

We wish to know, now, whether the solution of the equations (10) describes an electron with the spin properties that electrons are observed to have. It is known that the ground state of the hydrogen atom is degenerate, and that the energy splits into two in a magnetic field. We have to see whether this behaviour is predicted by the theory.

We see at once that the ground state is degenerate, the constants A and B being arbitrary. To find out what happens in a magnetic field we must solve the equations (10) for an electron in the field of a nucleus and in a magnetic field H . We shall find that the degeneracy is then removed. If the magnetic field is along the z -axis, then one solution is given by (11) with

$$A = 0, \quad B = 1.$$

This solution has energy $W_0 - MH$. We denote this solution by ψ_λ^I . The other solution ψ_λ^{II} has energy $W_0 + MH$ and is given by (11) with

$$A = 1, \quad B = 0.$$

This is shown in § 4.

If the magnetic field does not lie along the z -axis, then the two solutions may either be found directly as above, or from a consideration of the way in which the functions transform under a change of axes.† If the direction of the magnetic field is given by the polar angles θ , ϕ , then the solution with energy $W_0 - MH$ is given by (11) with

$$A = -\sin \frac{1}{2}\theta, \quad B = e^{i\phi} \cos \frac{1}{2}\theta.$$

The solution is therefore $A\psi_\lambda^I + B\psi_\lambda^{II}$.

This therefore is the wave function that describes an atom prepared with its magnetic moment pointing in the direction θ , ϕ . If the atom were then placed in a magnetic field along the z -axis, then clearly $|A|^2$ would give the probability that the atom should take up energy $+MH$, and $|B|^2$ the probability that it should take up energy $-MH$.

We have now shown that for slow electrons the Dirac treatment becomes identical with the non-relativistic Pauli-Darwin treatment. It is convenient to summarize here the two notations. In the Pauli-Darwin treatment an electron prepared with its axis in the direction \mathbf{l} (polar angles θ , ϕ) is described by a wave function

$$\psi(\mathbf{x}, \mathbf{y}, z)\chi_l(\mathbf{s}).$$

† Cf. Darwin, loc. cit.

ψ is the ordinary solution of Schrödinger's equation; HM_s is the energy that the electron would have due to a magnetic field H along the z -axis. χ vanishes unless $s = \pm 1$ and then

$$\begin{aligned}\chi &= e^{i\phi} \cos \frac{1}{2}\theta \quad (s = -1), \\ \chi &= -\sin \frac{1}{2}\theta \quad (s = +1).\end{aligned}$$

In Dirac's notation the electron is described by a wave function

$$\psi_\lambda(x, y, z) \quad (\lambda = 1, 2, 3, 4).$$

ψ_1 and ψ_2 are negligible for slow electrons; ψ_3 and ψ_4 are multiples of ψ , and

$$\begin{aligned}\psi_3 &= -\sin \frac{1}{2}\theta \psi, \\ \psi_4 &= e^{i\phi} \cos \frac{1}{2}\theta \psi.\end{aligned}$$

$|\psi_4|^2 dx dy dz$ gives the probability that the electron is in the volume-element $dx dy dz$, and that the electron magnet would have energy $-MH$ in a magnetic field.

The fact that for slow electrons each of the functions ψ_3 and ψ_4 is approximately a solution of Schrödinger's equation provides a proof of the assumption made in § 2, that an electron can be ejected from one atom and captured by another atom without losing its spin direction. The spin direction will not in general change much unless the forces acting on the electron are such as to give it a velocity comparable with that of light.

3.1. *Treatment of the equations when the velocity of the electrons is comparable with that of light*

The exact solution of the equations (10) representing an electron moving in free space with momentum (p_1, p_2, p_3) and energy W has been given by Darwin,[†] and is

$$\begin{aligned}\psi_1 &= -\frac{Ap_3 + B(p_1 - ip_2)}{mc + W/c} S, & \psi_2 &= -\frac{A(p_1 + ip_2) - Bp_3}{mc + W/c} S, \\ \psi_3 &= AS, & \psi_4 &= BS,\end{aligned} \quad (12)$$

where $p_1^2 + p_2^2 + p_3^2 = \frac{W^2}{c^2} - m^2c^2$.

Here S denotes $\exp\{2\pi i(p_1x + p_2y + p_3z - Wt)/h\}$, and A and B are arbitrary constants. The number of electrons per unit volume described by this solution is

$$(AA^* + BB^*)2W/(W + mc^2).$$

We must now ask what relationship the constants A and B in (12) have

[†] Loc. cit.

to the direction of the spin axis. We have seen *that for the case* $v/c \ll 1$ this direction is given by the polar angles θ, ϕ , where

$$-B/A = \cot \frac{1}{2}\theta e^{i\phi}. \quad (13)$$

For a fast electron, however, we have yet to define what is meant by the direction of the spin axis—i.e. how it could be measured.

Two methods are possible; we may either suppose that the ‘observer’ is moving with the electron, and inquire in what direction the spin of the electron is pointing relative to *his* axes; or we may suppose that the electron is brought nearly to rest by an electric field, and inquire what the direction of its spin axis is then. The first question has been considered by Darwin,† who finds that equation (13) defines the direction of the spin axis relative to the *moving* observer. The second, however, is the method by which the spin might be observed in practice; we find that equation (13) defines the direction of the spin when the electron has been reduced to rest. This may be seen as follows.

We confine ourselves to the case of an electron moving parallel to the z -axis, there being also an electrostatic field in this direction. The equations (10) reduce to two equations in ψ_2, ψ_4 and two equations in ψ_1, ψ_3 . Eliminating ψ_2 between the first two of these, we obtain

$$\frac{2\pi i}{\hbar} \left(\frac{W + \epsilon V}{c} - mc \right) \psi_4 - \frac{\partial}{\partial z} \left[\frac{\hbar}{2\pi i} \left(\frac{W + \epsilon V}{c} + mc \right) \frac{\partial \psi_4}{\partial z} \right] = 0$$

and ψ_3 satisfies exactly the same equation. Thus, since ψ_3 and ψ_4 both satisfy the same boundary conditions, it follows that

$$\psi_3/\psi_4 = \text{const.}$$

Hence, as the velocity of the electron decreases, the ratio B/A does not change. Thus (13) gives the direction of the spin axis when the electrons are brought to rest by the field.

3.2. Nature of an unpolarized beam

A *slow* unpolarized beam is one in which the electron spins point in all directions at random. It is not possible to represent an unpolarized beam by a single wave; each electron must be given its separate wave function, with different values of the constants A and B .

A *fast* unpolarized beam is the beam produced from a slow beam by accelerating it by means of an electric field. It follows from the results of the last section that such a beam would appear unpolarized to a moving observer relative to whom the electrons were at rest.

We shall now show that a beam in which half the electrons have

† *Proc. Roy. Soc. A*, **120** (1928), 628, § 5.

been prepared with their axes pointing in a given direction, and the other half with their axes pointing in the opposite direction, behaves like an unpolarized beam. To make the discussion definite we shall suppose that a beam of electrons travelling in the direction (l, m, n) passes into any electromagnetic field. The beam will be represented by a wave function $\psi_\lambda(x, y, z)\exp(-2\pi i Wt/h)$. In the part of space where the beam is before passing into the field, ψ_λ must have the form of a plane wave, moving in the direction (l, m, n) and polarized in some definite direction. Let (X, Y, Z) be some point in space where the beam arrives after it has passed the field, so that

$$P = \sum_{\lambda} |\psi_\lambda(X, Y, Z)|^2$$

gives the probability that an electron will be found at this point. We have to show that if P be averaged over all initial directions of the spin axis, the same result is obtained as by taking the average value of P for two opposite directions.

In the last section it was shown that a plane wave in which the spin axis points along the z -axis is represented by

$$\psi_3 = 0, \quad \psi_4 = S,$$

and that a plane wave in which the spin axis points in the opposite direction is represented by

$$\psi_3 = S, \quad \psi_4 = 0.$$

Let $\psi_\lambda^I, \psi_\lambda^{II}$ be the wave functions which have these forms in the part of space occupied by the incident wave. Then the wave function which describes an electron with spin initially in the direction (θ, ϕ) is

$$-\sin \frac{1}{2}\theta \psi_\lambda^I + \cos \frac{1}{2}\theta e^{i\phi} \psi_\lambda^{II}.$$

Thus

$$P = \sin^2 \frac{1}{2}\theta \sum_{\lambda} |\psi_\lambda^I|^2 + \cos^2 \frac{1}{2}\theta \sum_{\lambda} |\psi_\lambda^{II}|^2 - \sum_{\lambda} \sin \theta \cos(\phi + \alpha_\lambda) D_\lambda,$$

where we write

$$\psi_\lambda^{II}(\psi_\lambda^I)^* = D_\lambda e^{i\alpha_\lambda}.$$

If we take the opposite direction to θ, ϕ , namely,

$$\pi - \theta, \quad \pi + \phi,$$

we obtain

$$P = \cos^2 \frac{1}{2}\theta \sum_{\lambda} |\psi_\lambda^I|^2 + \sin^2 \frac{1}{2}\theta \sum_{\lambda} |\psi_\lambda^{II}|^2 + \sum_{\lambda} \sin \theta \cos(\phi + \alpha_\lambda) D_\lambda.$$

The mean of these is $\frac{1}{2} \sum_{\lambda} [|\psi_\lambda^I|^2 + |\psi_\lambda^{II}|^2]$.

Clearly the same result is obtained if P is averaged over all θ, ϕ .

3.3. The magnetic moment of an atom according to Dirac's equation

Our purpose in this section is to show that an electron in the lowest quantum state, in the field of a nucleus of charge $Z\epsilon$, and a magnetic field H along the z -axis, has energy, according to Dirac's equation,

$$W_0 \pm HM,$$

where W_0 is the energy in the absence of a field, and

$$M = \frac{\epsilon\hbar}{4\pi mc} \frac{1}{2} [1 + 2(1 - \gamma^2)^{\frac{1}{2}}] \quad (\gamma = 2\pi Z\epsilon^2/\hbar c).$$

It will further be shown that, when the atom is in the state with energy $-HM$ (spin pointing along the z -axis), the wave function ψ_λ describing the electron is such that $\psi_3 = 0$.

The wave equation for the electron is (cf. equation 10)

$$\left[\frac{W + \epsilon V}{c} + \sum_{t=1}^3 \alpha_t \left(p_t + \frac{\epsilon A_t}{c} \right) + \alpha_4 mc \right] \psi = 0,$$

where W is the energy, α_t , α_4 are the usual matrices, $V = Z\epsilon/r$, and A_t is given by

$$A_1 = -\frac{1}{2}Hy, \quad A_2 = \frac{1}{2}Hx, \quad A_3 = 0.$$

One can thus write the wave equation

$$(W + \epsilon V - U + c \sum \alpha_t p_t + \alpha_4 mc^2) \psi = 0,$$

where U is the perturbing energy due to the magnetic field, namely,

$$U = -\epsilon(\alpha_1 A_1 + \alpha_2 A_2).$$

For the case $H = 0$ the lowest state is degenerate. There are two solutions, which we denote by ψ^I and ψ^{II} . If we write

$$f(r) = Ar^\beta e^{-r/a},$$

where

$$\beta = (1 - \gamma^2)^{\frac{1}{2}} - 1,$$

and A is so chosen that

$$4\pi \int_0^\infty |f(r)|^2 r^2 dr = 1,$$

then these solutions, normalized to unity, are†

$$\left. \begin{aligned} \psi_1^I &= iNB \sin \theta e^{i\phi} f \\ \psi_2^I &= -iNB \cos \theta f \\ \psi_3^I &= 0 \\ \psi_4^I &= Nf \end{aligned} \right\} \quad (\text{I})$$

† Darwin, *Proc. Roy. Soc. A*, 118 (1928), 654.

and

$$\left. \begin{aligned} \psi_1^{\text{II}} &= -iNB \cos \theta f \\ \psi_2^{\text{II}} &= -iNB \sin \theta e^{i\phi} f \\ \psi_3^{\text{II}} &= Nf \\ \psi_4^{\text{II}} &= 0 \end{aligned} \right\}, \quad (\text{II})$$

where $B = \gamma[1 + (1 - \gamma^2)^{\frac{1}{2}}]^{-1}$, $(B^2 + 1)N^2 = 1$.

It is easily seen that $\int \psi^{\text{I}} \psi^{\text{II}} dx dy dz = 0$.

For the energy values in a magnetic field we solve by the usual perturbation method. If therefore ΔW is the change of energy produced by the field, we obtain

$$\begin{vmatrix} \Delta W - U^{\text{I,I}} & -U^{\text{II,I}} \\ -U^{\text{I,II}} & \Delta W - U^{\text{II,II}} \end{vmatrix} = 0,$$

where $U^{\text{I,II}} = \int \bar{\psi}^{\text{I}} U \psi^{\text{II}} dx dy dz$, etc.

It is easily seen that the non-diagonal elements $U^{\text{I,II}}$ vanish; thus ψ^{I} and ψ^{II} are the correct zero-order wave functions, and $U^{\text{II,II}}$ is the change of energy when the atom is in the state described by the wave function ψ^{II} .

We shall evaluate $U^{\text{II,II}}$. We have

$$\begin{aligned} \bar{\psi}^{\text{II}} \alpha_1 \psi^{\text{II}} &= \bar{\psi}_1 \psi_4 + \bar{\psi}_2 \psi_3 + \bar{\psi}_3 \psi_2 + \bar{\psi}_4 \psi_1 \\ &= 2N^2 B \sin \theta \sin \phi f^2. \end{aligned}$$

Hence $\frac{1}{2} \epsilon H y \bar{\psi}^{\text{II}} \alpha_1 \psi^{\text{II}} = \epsilon H N^2 B \sin^2 \theta \sin^2 \phi r f^2$.

Similarly, we find that

$$-\frac{1}{2} \epsilon H x \bar{\psi}^{\text{II}} \alpha_2 \psi^{\text{II}} = \epsilon H N^2 B \sin^2 \theta \cos^2 \phi r f^2.$$

Thus, adding and integrating over all space, we have

$$U^{\text{II,II}} = \epsilon H N^2 B \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 dr \sin^2 \theta r f^2.$$

Evaluating this integral, we obtain

$$U^{\text{II,II}} = \frac{\epsilon h H}{4\pi m c} \frac{1}{3} [1 + 2(1 - \gamma^2)^{\frac{1}{2}}],$$

which is the change of energy due to H when the atom is in the state II. Similarly we find that $U^{\text{I,I}}$ is equal to *minus* the same quantity.

The factor $\frac{1}{3} [2(1 - \gamma^2)^{\frac{1}{2}} + 1]$ tends to 1 as $\gamma \rightarrow 0$. For uranium it is 0.83.

4. The scattering of electrons by a centre of force

We now consider the way in which the discussion of Chapter II must be modified when the motion of the particles concerned is determined by Dirac's equations instead of the Schrödinger equation.

The wave function ψ describing the scattering now has four components ψ_1, \dots, ψ_4 , which have the asymptotic forms

$$\psi_\lambda = a_\lambda e^{ikz} + r^{-1} e^{ikr} u_\lambda(\theta, \phi) \quad (\lambda = 1, 2, 3, 4). \quad (14)$$

The differential cross-section $I(\theta, \phi) d\omega$ is now given by

$$I(\theta, \phi) d\omega = \left\{ \sum_1^4 |u_\lambda(\theta, \phi)|^2 / \sum_1^4 |a_\lambda|^2 \right\} d\omega. \quad (15)$$

The quantities a_λ are not all independent. Referring to the solutions (12) for a plane wave, it will be seen that, when $p_1 = p_2 = 0$, $p_3 = k\hbar$,

$$\left| \frac{a_1}{a_3} \right| = \frac{k\hbar c}{W + mc^2} = \left| \frac{a_2}{a_4} \right|, \quad (16)$$

no matter what orientation the spin axis may have. The same relation exists between the u_λ for, asymptotically, the scattered wave may be regarded as made up of a number of plane waves proceeding outward from the centre in different directions. We may therefore write

$$I(\theta, \phi) d\omega = \frac{|u_3|^2 + |u_4|^2}{|a_3|^2 + |a_4|^2} d\omega. \quad (17)$$

In practice the incident electron beam will normally be unpolarized. As such a beam may be regarded as made up of equal numbers of electrons with spins respectively parallel and antiparallel to the direction of propagation, we first consider the scattering in these two particular cases. The asymptotic forms of the components ψ_3, ψ_4 are

$$\left. \begin{aligned} \psi_3 &\sim e^{ikz} + r^{-1} e^{ikr} f_1(\theta, \phi) \\ \psi_4 &\sim r^{-1} e^{ikr} g_1(\theta, \phi) \end{aligned} \right\} \text{(A)} \\ \left. \begin{aligned} \psi_3 &\sim r^{-1} e^{ikr} g_2(\theta, \phi) \\ \psi_4 &\sim e^{ikz} + r^{-1} e^{ikr} f_2(\theta, \phi) \end{aligned} \right\} \text{(B)} \quad (18)$$

for the two cases, (B) referring to electrons with spins parallel and (A) with spins antiparallel, to the direction of incidence. To obtain the functions f_1, f_2, g_1, g_2 use may be made of the sets of solutions found by Darwin† of the equations (10) with the scalar scattering potential V a function of r only and the vector potential zero. He gives the groups of solutions

† *Proc. Roy. Soc. A*, **118** (1928), 654.

$$\begin{aligned}
 \left. \begin{aligned}
 \psi_3 &= (n+1)G_n P_n(\cos \theta), & \psi_4 &= -G_n P_n^1(\cos \theta)e^{i\phi} \\
 \psi_3 &= nG_{-n-1} P_n(\cos \theta), & \psi_4 &= G_{-n-1} P_n^1(\cos \theta)e^{i\phi} \\
 \psi_3 &= G_n P_n^1(\cos \theta)e^{i\phi}, & \psi_4 &= (n+1)G_n P_n(\cos \theta) \\
 \psi_3 &= -G_{-n-1} P_n^1(\cos \theta)e^{i\phi}, & \psi_4 &= nG_{-n-1} P_n(\cos \theta)
 \end{aligned} \right\} \begin{array}{l} \text{(A)} \\ \text{(B)} \end{array} \quad (19)
 \end{aligned}$$

where G_n is a solution of the simultaneous equations

$$\begin{aligned}
 \frac{1}{\hbar} \left(\frac{W}{c} - \frac{\epsilon V}{c} + mc \right) F_n + \frac{dG_n}{dr} - \frac{n}{r} G_n &= 0, \\
 -\frac{1}{\hbar} \left(\frac{W}{c} - \frac{\epsilon V}{c} - mc \right) G_n + \frac{dF_n}{dr} + \frac{n+2}{r} F_n &= 0,
 \end{aligned} \quad (20)$$

and G_{-n-1} is a solution of a similar pair of equations with $-n-1$ in place of n .

By elimination of the function F_n we have

$$\frac{d^2 G_n}{dr^2} + \left(2 - \frac{\alpha'}{\alpha} \right) G_n + \left\{ \alpha \beta - \frac{n(n+1)}{r^2} + \frac{n}{r} \frac{\alpha'}{\alpha} \right\} G_n = 0, \quad (21)$$

where

$$\alpha = \frac{1}{\hbar} \left(\frac{W}{c} - \frac{\epsilon V}{c} + mc \right), \quad \beta = \frac{1}{\hbar} \left(\frac{W}{c} - \frac{\epsilon V}{c} - mc \right).$$

The substitution $G_n = \alpha^{\frac{1}{2}} \mathcal{G}_n / r$

brings the equation into the Schrödinger form (12) of Chapter II, viz.

$$\frac{d^2 \mathcal{G}_n}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} - U_n(r) \right] \mathcal{G}_n = 0, \quad (22)$$

with

$$U_n(r) = -\frac{2W}{\hbar^2 c^2} \epsilon V + \frac{1}{\hbar^2} \frac{\epsilon^2 V^2}{c^2} + \frac{n+1}{r} \frac{\alpha'}{\alpha} - \frac{3}{4} \frac{\alpha'^2}{\alpha^2} + \frac{1}{2} \frac{\alpha''}{\alpha}, \quad (23)$$

$$k^2 = (W^2 - m^2 c^4) / \hbar^2 c^2.$$

A similar result follows for \mathcal{G}_{-n-1} with $-n-1$ in place of n .

Of the terms appearing in the expression (23) for $U_n(r)$ the first two are independent of the electron spin and are typical of the Klein-Gordon equation for a particle without spin. The remaining terms are a consequence of spin-orbit interaction and depend, not only on the potential, but also on the force and its radial derivative.

It follows that the proper solutions G_n, G_{-n-1} of (20) can be taken to have the asymptotic forms

$$\begin{aligned}
 G_n &\sim r^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n), \\
 G_{-n-1} &\sim r^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_{-n-1}).
 \end{aligned} \quad (24)$$

By combining the solutions (19A) in the following way we obtain functions ψ_3, ψ_4 having the asymptotic forms (18A):

$$\begin{aligned}\psi_3 &= \sum_{n=0}^{\infty} \{(n+1)e^{i\eta_n}G_n + ne^{i\eta_{-n-1}}G_{-n-1}\}i^n P_n(\cos \theta), \\ \psi_4 &= \sum_{n=1}^{\infty} \{-e^{i\eta_n}G_n + e^{i\eta_{-n-1}}G_{-n-1}\}i^n P_n^1(\cos \theta)e^{i\phi}.\end{aligned}\tag{25}$$

From these we have

$$\begin{aligned}f_1(\theta, \phi) &= \frac{1}{2ik} \sum \{(n+1)(e^{2i\eta_n} - 1) + n(e^{2i\eta_{-n-1}} - 1)\}P_n(\cos \theta), \\ g_1(\theta, \phi) &= \frac{1}{2ik} \sum \{-e^{2i\eta_n} + e^{2i\eta_{-n-1}}\}P_n^1(\cos \theta)e^{i\phi}.\end{aligned}\tag{26}$$

By comparison with (17) of Chapter II we see that the non-relativistic case is obtained by taking $\eta_n = \eta_{-n-1}$.

For the case (B) of parallel spin we find, by a similar procedure, that

$$f_2(\theta, \phi) = f_1(\theta, \phi) = f(\theta), \quad \text{say,}$$

and that

$$g_2(\theta, \phi) = -g(\theta)e^{-i\phi},$$

where

$$g_1(\theta, \phi) = g(\theta)e^{i\phi}.\tag{27}$$

The general case of arbitrary initial spin direction for which the incident wave is given by

$$\psi_3 = Ae^{ikz}, \quad \psi_4 = Be^{ikz},$$

may now be obtained by linear combination, to give

$$u_3 = Af - Bge^{-i\phi},$$

$$u_4 = Bf + Age^{i\phi},$$

so that

$$I(\theta) = |f|^2 + |g|^2 + (fg^* - gf^*) \left(\frac{-AB^*e^{i\phi} + A^*Be^{-i\phi}}{|A|^2 + |B|^2} \right).\tag{28}$$

4.1. Polarization

Referring to (28) we see that the scattering of a partially polarized beam depends, not only on θ , but also on ϕ . Thus, in Fig. 11, the intensity scattered in the direction CD would not be the same as in the direction CE . An effect of this sort would be observed in a double scattering experiment as follows. Referring to Fig. 11, an unpolarized beam of electrons is incident on a target B . That portion which is scattered in the direction BC is incident on a second target C . This scattered beam is partially polarized by the scattering at B , for electrons with spins parallel and antiparallel are not in general affected in the

same way by the scattering field. As a result those beams which suffer a second scattering into the directions CD , CE respectively, both making the same angle θ_2 with BC , will not be of equal intensity.

The detailed theory of such a double scattering experiment was first worked out by Mott.† We consider, as usual, the incident unpolarized beam as made up of equal numbers of electrons with spins parallel and antiparallel to the direction of incidence.

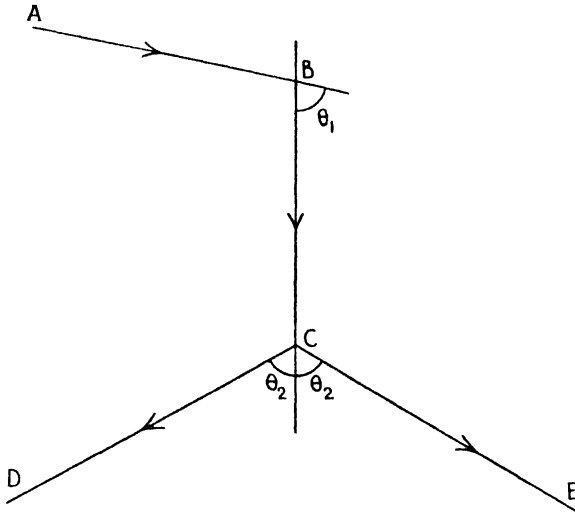


FIG. 11.

For those electrons with spins antiparallel we have, in the incident beam,

$$\psi_3 = Ae^{ikz}, \quad \psi_4 = 0, \quad AA^* = \frac{1}{2}.$$

After the first scattering through an angle θ_1 , in the plane $\phi = 0$ (the plane of ABC in Fig. 11) the components of the wave function will be proportional to $Af_1(\theta_1)$, $Ag_1(\theta_1)$. We now rotate the axes through an angle θ_1 , so that the z -axis is along BC , ABC remaining the plane $\phi = 0$. The components of the scattered beam, referred to these new axes, become, apart from the term e^{ikz} and a constant factor,

$$\psi_3 = A(f_1 \cos \frac{1}{2}\theta_1 + g_1 \sin \frac{1}{2}\theta_1), \quad \psi_4 = A(g_1 \cos \frac{1}{2}\theta_1 - f_1 \sin \frac{1}{2}\theta_1). \quad (29)$$

Substituting these values in place of A and B respectively in (28), we obtain the intensity $|u_3|^2 + |u_4|^2$ of the second scattering. In the same way we may obtain the contribution from the electrons in the incident beam with spins parallel to the incident direction. Adding the two

† *Proc. Roy. Soc. A*, **124** (1929), 425 and **135** (1932), 429.

gives for the intensity scattered in the direction (θ_2, ϕ_2)

$$\{|f(\theta_1)|^2 + |g(\theta_1)|^2\}\{|f(\theta_2)|^2 + |g(\theta_2)|^2 + 2D(\theta_1)D(\theta_2)\cos\phi_2\}, \quad (30)$$

where

$$D(\theta) = i(fg^* - gf^*).$$

This formula shows that, for a fixed value of θ_1 and θ_2 , the scattered intensity depends on ϕ_2 through the factor

$$1 + \delta \cos \phi_2,$$

where

$$\delta = \frac{2D(\theta_1)D(\theta_2)}{\{|f(\theta_1)|^2 + |g(\theta_1)|^2\}\{|f(\theta_2)|^2 + |g(\theta_2)|^2\}}. \quad (31)$$

When $D(\theta) = 0$ the effect vanishes. In this case all the initial spin directions are rotated through the same angle by the scattering so that an unpolarized beam remains unpolarized.

In general the asymmetry will be small when $D(\theta)$ is small, although it may have isolated large values under special conditions for which the denominator is very small. $D(\theta)$ will be small, in general, when g is small, *i.e.* in the non-relativistic limit. Referring to (26, 27) we see that

$$g = -\frac{1}{k} \sum_n P_n^1(\cos\theta) \sin \chi_n e^{2i\delta_n}, \quad (32)$$

where

$$\chi_n = \eta_n - \eta_{-n-1}, \quad 2\delta_n = \eta_n + \eta_{-n-1}.$$

The phases η_n, η_{-n-1} are determined from the equation (22) for \mathcal{G}_n and the corresponding one for \mathcal{G}_{-n-1} . These differ in one term only, that involving $r^{-1}\alpha'/\alpha$, which appears multiplied by $n+1$ and by $-n$ for $\mathcal{G}_n, \mathcal{G}_{-n-1}$ respectively. As α' is proportional to dV/dr we see that the phase differences, χ_n , and hence the function $D(\theta)$ and the asymmetry, are determined by the force rather than by the potential of the scattering centre.

4.2. *The case of the Coulomb field*

We now consider the scattering of fast electrons by an unshielded atomic nucleus of charge $Z\epsilon$ so that $V = -Z\epsilon/r$. As for the non-relativistic case discussed in Chapter III, the slow decrease of this potential with distance modifies the asymptotic form of the functions G_n, G_{-n-1} . The formulae (26) and (27) still hold with the phases η_n, η_{-n-1} such that

$$G_{n,-n-1} \sim r^{-1} \sin(kr + \gamma \log 2kr - \frac{1}{2}n\pi + \eta_{n,-n-1}), \quad (33)$$

where $\gamma = 2\pi Z\epsilon^2/\hbar v$.

The equations (20) for G_{-n-1} , now take the form

$$\begin{aligned} \frac{1}{\hbar} \left(\frac{W}{c} + \frac{Z\epsilon^2}{rc} + mc \right) F_{-n-1} + \frac{dG_{-n-1}}{dr} + \frac{(n+1)}{r} G_{-n-1} &= 0, \\ -\frac{1}{\hbar} \left(\frac{W}{c} + \frac{Z\epsilon^2}{rc} - mc \right) G_{-n-1} + \frac{dF_{-n-1}}{dr} - \frac{(n-1)}{r} F_{-n-1} &= 0. \end{aligned} \quad (34)$$

Writing

$$\begin{aligned} rF_{-n-1} &= \left(1 - \frac{W}{mc^2} \right)^{\frac{1}{2}} (\sigma_1 - \sigma_2), \\ rG_{-n-1} &= \left(1 + \frac{W}{mc^2} \right)^{\frac{1}{2}} (\sigma_1 + \sigma_2), \end{aligned}$$

we have then

$$\begin{aligned} \frac{d\sigma_1}{dr} &= -i \left(k + \frac{\gamma}{r} \right) \sigma_1 - (n + i\gamma') \frac{\sigma_2}{r}, \\ \frac{d\sigma_2}{dr} &= - (n - i\gamma') \frac{\sigma_1}{r} + i \left(k + \frac{\gamma}{r} \right) \sigma_2, \end{aligned}$$

where

$$\gamma' = \left(1 - \frac{v^2}{c^2} \right)^{\frac{1}{2}} \gamma, \quad k^2 = \frac{4\pi^2}{\hbar^2} \left(\frac{W^2}{c^2} - m^2 c^2 \right).$$

Expanding σ_1, σ_2 in the power series

$$\sigma_1 = e^{-ikr} r^s \sum a_\nu r^\nu, \quad \sigma_2 = e^{-ikr} r^s \sum b_\nu r^\nu,$$

we find that the regular solutions are expressible in the form

$$\begin{aligned} \sigma_1 &= a_0 e^{-ikr} r^{\rho_n} F(i\gamma + \rho_n, 2\rho_n + 1, 2ikr), \\ \sigma_2 &= b_0 e^{-ikr} r^{\rho_n} F(i\gamma + \rho_n + 1, 2\rho_n + 1, 2ikr), \end{aligned}$$

where

$$\frac{a_0}{b_0} = -\frac{i\gamma - \rho_n}{i\gamma' - n}, \quad \rho_n = (n^2 - \alpha^2)^{\frac{1}{2}}, \quad \alpha = \gamma \frac{v}{c} = 2\pi Z\epsilon^2 / hc.$$

This gives

$$\begin{aligned} G_{-n-1} &= N_{-n-1} (2kr)^{\rho_n} r^{-1} e^{-ikr} \times \\ &\times \{ -(n - i\gamma') F(i\gamma + \rho_n + 1, 2\rho_n + 1, 2ikr) + \\ &\quad + (\rho_n - i\gamma) F(\rho_n + i\gamma, 2\rho_n + 1, 2ikr) \}, \end{aligned} \quad (35)$$

where N_{-n-1} is a constant. Using the asymptotic expressions given in Chap. III, § 3, for the hypergeometric functions, we find that

$$G_{-n-1} \sim r^{-1} \sin(kr + \gamma \log 2kr - \frac{1}{2}n\pi + \eta_{-n-1}), \quad (36)$$

where

$$\exp(2i\eta_{-n-1}) = \frac{n - i\gamma'}{\rho_n - i\gamma} \frac{\Gamma(\rho_n + 1 - i\gamma)}{\Gamma(\rho_n + 1 + i\gamma)} \exp\{-\pi i(\rho_n - n)\}, \dagger \quad (37)$$

the constant N_{-n-1} being then given by

$$N_{-n-1} = \frac{1}{2} \frac{|\Gamma(\rho_n + 1 + i\gamma)|}{\Gamma(2\rho_n + 1)} \exp(\frac{1}{2}\pi\gamma) \{(i\gamma' - n)(\rho_n - i\gamma)\}^{-\frac{1}{2}}. \quad (38)$$

† Note that $\exp(2i\eta_n)$ is obtained from (37) by replacing n by $-n-1$ everywhere except in the last factor which becomes $\exp\{-\pi i(\rho_{n+1} - n)\}$.

Writing

$$C_n = -e^{-i\pi\rho_n} \frac{\Gamma(\rho_n - i\gamma)}{\Gamma(\rho_n + 1 + i\gamma)},$$

$$F(\theta) = \frac{1}{2}i \sum (-1)^n \{n C_n + (n+1) C_{n+1}\} P_n(\cos \theta),$$

$$G(\theta) = \frac{1}{2}i \sum (-1)^n \{n^2 C_n - (n+1)^2 C_{n+1}\} P_n(\cos \theta),$$
(39)

we now have, on substitution of (37) and the corresponding expression for $\exp(2i\eta_n)$ in (26) and (27),

$$kf(\theta) = -i\gamma' F + G,$$

$$kg(\theta) = [i\gamma'(1 + \cos \theta)F + (1 - \cos \theta)G]/\sin \theta.$$
(40)

The differential cross-section is, then,

$$|f|^2 + |g|^2 = \gamma'^2 |F|^2 / (k^2 \sin^2 \frac{1}{2}\theta) + |G|^2 / (k^2 \cos^2 \frac{1}{2}\theta).$$
(41)

Closed expressions for F and G cannot be obtained, but they may be expanded in powers of α to give an expression, valid for scattering by light elements since $\alpha = Z/137$.

In the limit $\gamma' = \gamma$, $\alpha^2 = 0$ we must recover the case of scattering by a Coulomb field when spin and relativistic effects are ignored. Referring to Chap. III (16) it follows that, in this case,

$$kf(\theta) \rightarrow R \operatorname{cosec}^2 \frac{1}{2}\theta, \quad g(\theta) \rightarrow 0,$$

where

$$R = \frac{1}{2}\gamma \exp \left[2i\gamma \log \sin \frac{1}{2}\theta + \arg \frac{\Gamma(1 - i\gamma)}{\Gamma(1 + i\gamma)} + i\pi \right].$$

Hence, if we expand F and G in powers of α ,

$$F = F_0 + \alpha F_1 + \alpha^2 F_2 + \dots,$$

$$G = G_0 + \alpha G_1 + \alpha^2 G_2 + \dots,$$

we must have, from (40), when $\gamma' = \gamma$,

$$F_0 = iR/\gamma, \quad G_0 = R \cot^2 \frac{1}{2}\theta.$$

Since F and G do not contain γ , we obtain, on substitution in (41), the differential cross-section

$$\frac{Z^2 e^4}{4m^2 v^4 \sin^4 \frac{1}{2}\theta} \left(1 - \frac{v^2}{c^2} \sin^2 \frac{1}{2}\theta \right) \left(1 - \frac{v^2}{c^2} \right),$$
(42)

which is valid for all values of v , provided α is small compared with unity.

To this approximation the Rutherford scattering formula must be multiplied by $(1 - v^2/c^2)\{1 - (v^2/c^2) \sin^2 \frac{1}{2}\theta\}$, the first factor arising from the Lorentz contraction, the second from the effect of the spin. As, according to this approximation, both f and g are real, apart from the common phase factor $\exp(2i\gamma \log \sin^2 \frac{1}{2}\theta)$, no asymmetry would be observed on

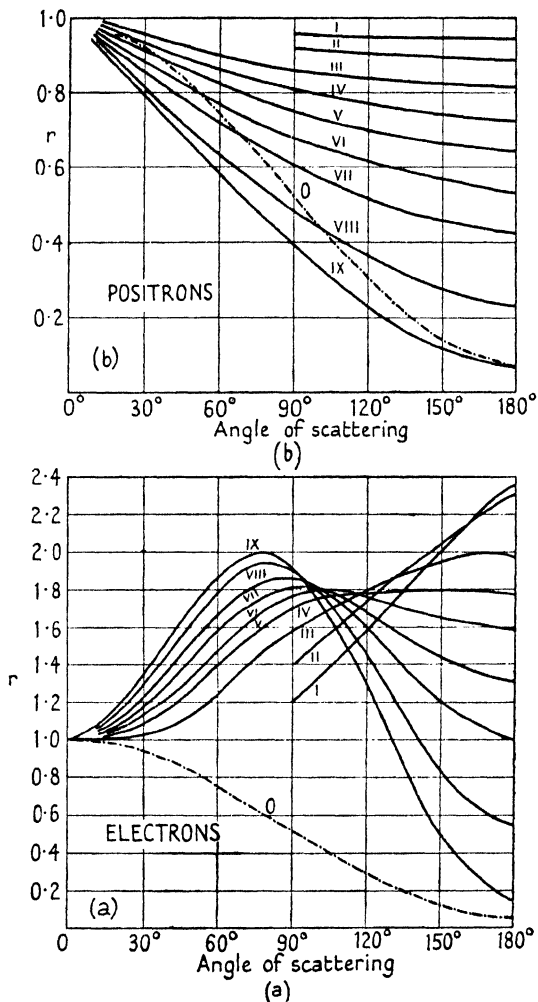


FIG. 12. Angular distributions of electrons and of positrons of various energies scattered by mercury nuclei. The scattered intensity is given as the ratio r to that given by the formula

$$\frac{Z^2 e^4}{m^2 v^4} \operatorname{cosec}^4 \frac{1}{2} \theta (1 - v^2/c^2).$$

Curves I-IX respectively correspond to particles of energies 0.046, 0.086, 0.145, 0.232, 0.314, 0.463, 0.666, 1.28, and $3.35 mc^2$.

Curve 0 is that given by the approximate formula (42) for an energy of $3.35 mc^2$.

12(a) electrons; 12(b) positrons.

double scattering. To obtain a finite value for the quantity δ of (31) it is necessary to proceed to the next approximation. This has been done by Mott,† who finds that, for $\theta_1 = \theta_2 = 90^\circ$,

$$\delta \simeq \left(\frac{Z}{137}\right)^2 \frac{\{1 - (v^2/c^2)\}(v^2/c^2)}{\{2 - (v^2/c^2)\}^2}, \quad (43)$$

having a minimum value of $0.2(Z/137)^2$ for $v/c = 0.81$. To the same approximation the differential cross-section (17) includes the factor‡

$$\left(1 - \frac{v^2}{c^2} \sin^2 \frac{1}{2}\theta + \alpha \frac{v}{c} \sin \frac{1}{2}\theta\right)$$

in place of

$$1 - \frac{v^2}{c^2} \sin^2 \frac{1}{2}\theta.$$

For scattering by heavy elements $Z/137$ is not small and the approximate expressions (42) and (43) are no longer valid. Numerical values for the differential cross-section and the asymmetry factor were first obtained from the exact expressions (40) by Mott.§ In 1932 he evaluated δ as a function of v/c for double scattering at 90° by gold nuclei and also gave the differential cross-sections for single scattering at this angle. Bartlett and Watson|| have since carried out calculations for mercury nuclei from which they give the differential cross-sections as a function of v/c for single scattering at 90° . Fig. 12(a) illustrates their results for the single scattering cross-sections. It is convenient to give these in terms of the ratio r of the scattering to that given by the Rutherford formula

$$\frac{Z^2 \epsilon^4}{4m^2 v^4} \operatorname{cosec}^4 \frac{1}{2}\theta (1 - v^2/c^2),$$

modified to allow only for the variation of mass with velocity. It will be seen that the approximate expression $\{1 - (v^2/c^2) \sin^2 \frac{1}{2}\theta\}$, given by (42) for r , is very inaccurate for heavy elements.

The variation of the asymmetry factor δ with electron velocity as found by Mott and by Bartlett and Watson is illustrated in Fig. 13. It will be seen that for v/c in the neighbourhood of 0.6 a considerable effect should be observed in a double scattering experiment. Although these results have been derived on the assumption of scattering by a bare nucleus, it has been shown†† that the effect of screening by the atomic electrons does not seriously affect the predicted value of δ .

† *Proc. Roy. Soc. A*, **124** (1929), 425.

‡ Urban, *Zeits. f. Physik*, **119** (1942), 67.

§ *Proc. Roy. Soc. A*, **135** (1932), 429.

|| *Proc. Am. Acad. Art. Sci.* **74** (1940), 53.

†† Massey and Mohr, *Proc. Roy. Soc. A*, **177** (1941), 341; Bartlett and Welton, *Phys. Rev.* **59** (1941), 281.

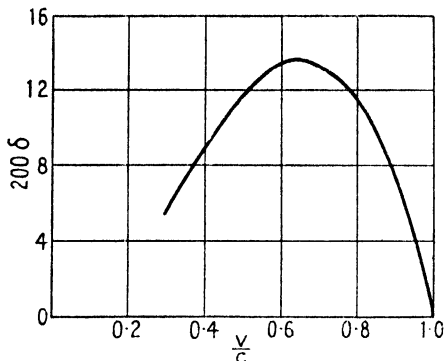


FIG. 13. Percentage asymmetry in double scattering of electrons at 90° by mercury nuclei.

4.3. Comparison with experiment

Although it cannot yet be said that the relativistic theory of scattering of fast electrons by atomic nuclei has been confirmed in detail by experiment, the most recent observations are in good agreement with its predictions.

The most recent experiment on single scattering of fast electrons are those of Bueckner, van der Graaf, and Feshbach.† They used cathode rays of energies ranging from 1.27 to 2.27 M.e.V. and measured the absolute intensity of scattering over an angular range from 20° to 50° . This was found to be in very good agreement with theoretical prediction for the scattering materials investigated—beryllium, aluminium, copper, silver, platinum, and gold. The results obtained prior to 1942 have been summarized by Urban.‡ They present a rather confused picture. Thus, good agreement with the theory has been found by Champion and Barber§ for the scattering of RaE β -rays (0.7–1.2 M.e.V. energy), by Fowler and Oppenheimer|| for 5.0–17 M.e.V. β -rays scattered by lead, by Saunderson and Duffendack†† for RaE β -rays scattered by copper, argon, and gold, by Gupta‡‡ for 2 M.e.V. β -rays scattered by xenon, and by Brailovsky and Leipunsky§§ for RaC β -rays scattered by argon. On the other hand, Champion and Barber§ found only 1/7th of the theoretical intensity for scattering of RaE β -rays by mercury, although the angular distribution was as predicted, and other investi-

† *Phys. Rev.* **69** (1946), 452. See also Bueckner, van der Graaf, Sperduto, Burrill, and Feshbach, *ibid.* **72** (1947), 678.

‡ *Zeits. f. Physik*, **119** (1942), 67.

§ *Proc. Roy. Soc. A*, **168** (1938), 159; *Phys. Rev.* **55** (1939), 111.

|| *Ibid.* **54** (1938), 320.

†† *Ibid.* **60** (1941), 190.

‡‡ *Proc. Phys. Soc.* **51** (1939), 355.

§§ *J. Phys. U.S.S.R.* **4** (1941), 485.

gators have found ratios of observed to theoretical intensities for scattering by nitrogen ranging from 0.5 to 9.† Some discrepancies have also been found in some recent experiments using β -rays.‡ The internal consistency of all the experimental results using β -rays is not good and it is likely that the discrepancies will largely disappear when radioactive sources are replaced by artificial ones of controlled energy, as in the experiments of van der Graaf and others mentioned above. It must be mentioned, however, that in some experiments the inelastic scattering and the probability of pair formation by fast electrons§ also exhibit

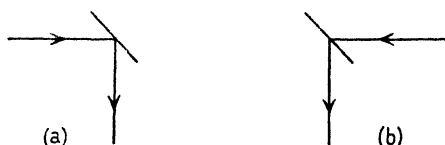


FIG. 14. Illustrating scattering at 90° by a foil in the 'reflection' and 'transmission' cases (a) and (b) respectively.

marked anomalies. More experiments are therefore required either to establish the theory once and for all or to reveal definitely the nature of any discrepancies.

Several attempts|| have been made to verify the predicted asymmetry in double scattering of electrons by gold nuclei. Until the work of Shull, Chase, and Myers†† these attempts were all unsuccessful. It is, of course, essential that, to reveal the asymmetry, the depolarizing effect of multiple scattering be avoided. Although the gold foils used as scatterers by Dymond and by Richter were thin enough for it to be possible to neglect multiple scattering involving a number of small deflexions, it appears that the probability of deflexion through 90° by two successive deflexions of comparable magnitude was not sufficiently small. This effect‡‡ is only marked when the electrons are scattered from the 'reflecting' side of the foil (case (a) in Fig. 14). In this case an electron deviated through 45° moves through the foil nearly parallel to its length and

† Stepanowa, *Phys. Zeit. Sow. Un.* **12** (1937), 550; Bothe and Ratzel, *Zeits. f. Physik*, **115** (1940), 497; Bosshard and Scherrer, *Helv. Phys. Acta*, **14** (1941), 85.

‡ Bleuler, Scherrer, and Zünti, *Phys. Rev.* **61** (1942), 95; Bleuler, *Helv. Phys. Acta*, **15** (1942), 613; du Pasquier, *ibid.* **17** (1944), 409; Sigrist, *ibid.* **16** (1943), 471.

§ See a summary by Champion, *Rep. Prog. Physics*, **5** (1939), 348.

|| Meyers, Byrne, and Cox, *Phys. Rev.* **46** (1943), 77; Dymond, *Proc. Roy. Soc. A*, **145** (1934), 657; Richter, *Ann. d. Physik*, **28** (1937), 533; Kikuchi, *Proc. Math. Phys. Soc. Jap.* **22** (1940), 805. The last author obtained results in agreement with theory, but he used such thick scatterers that multiple scattering must have been serious.

†† *Phys. Rev.* **63** (1943), 29.

‡‡ Chase and Cox, *ibid.* **58** (1940), 243; Goertzel and Cox, *ibid.* **63** (1943), 37; Petukhov and Vyshinsky, *J. Phys. U.S.S.R.* **5** (1941), 137.

therefore has a considerable chance of suffering a second deviation through 45° . On the other hand, in the 'transmission' case (*b*) of Fig. 14, either the first or second deviation must be through 135° and is very much less likely.

Dymond and Richter both observed scattering through angles of 90° from the reflecting sides of the foils for which the effect would be important. Shull, Chase, and Meyers confirmed the absence of an appreciable asymmetry under these conditions but observed, for the 400 k.e.V. beam of electrons they were using, a value for 200δ of 12 ± 0.2 when the two deflexions were of the transmission type. This agrees very well with the calculated value, as may be seen by reference to Fig. 13. Shull, Chase, and Meyers also checked that replacement of one of the gold foils by aluminium reduced the asymmetry very considerably, as would be expected.

On the whole, the evidence is thus in favour of the theory. Some further favourable evidence as far as small angle scattering is concerned will be discussed in Chap. IX, § 6, in connexion with multiple scattering.

5. The positron

In § 3.1 a set of solutions (12) representing an electron moving in free space with momentum (p_1, p_2, p_3) and energy W have been given. These are of the form

$$\psi_\lambda = a_\lambda \exp\left\{\frac{2\pi i}{h}(p_1 x + p_2 y + p_3 z - Wt)\right\} \quad (\lambda = 1, 2, 3, 4),$$

where
$$p_1^2 + p_2^2 + p_3^2 = \frac{W^2}{c^2} - m^2 c^2. \quad (44)$$

We have assumed the energy W to be positive, but there is nothing in the formalism which requires this. W must satisfy the relativistic momentum-energy relation (44). This gives

$$W = \pm c(p_1^2 + p_2^2 + p_3^2 - m^2 c^2)^{\frac{1}{2}},$$

and we have so far considered only the first of two alternatives. The second gives

$$\psi_\lambda = b_\lambda \exp\left\{\frac{2\pi i}{h}(p_1 x + p_2 y + p_3 z + Wt)\right\} \quad (\lambda = 1, 2, 3, 4),$$

with

$$b_1 = C, \quad b_2 = D, \quad b_3 = \frac{Cp_3 + D(p_1 - ip_2)}{mc + W/c},$$

$$b_4 = \frac{C(p_1 + ip_2) - Dp_3}{mc + W/c}. \quad (45)$$

This set of solutions corresponds to free electrons of negative kinetic energy, i.e. electrons of negative rest-mass.

Unless there are conditions which render these states inaccessible, electrons will tend to fall into them with release of energy in the form of radiation or kinetic energy of some other particle. On the other hand, no electrons of negative mass have ever been observed. To overcome this difficulty Dirac,† in 1930, suggested that all the states in which an electron possesses negative mass are already occupied by electrons, forming a distribution which is not observable because of its uniformity. Only 'holes' in the distribution, representing departures from uniformity, would be observed. Since the Pauli principle prevents two electrons from occupying the same quantum state, this theory successfully accounted for the failure of electrons with negative mass to appear in nature and also for the normal absence of transitions to these states. Furthermore, a vacant state in the distribution of negative mass electrons would appear as a particle with positive mass and positive charge. It was first suggested that this particle might be the proton, but Oppenheimer‡ in 1930 showed that its mass must be equal to that of a normal electron. Such particles were first observed by Anderson in 1932§ among the secondary particles produced by cosmic rays, a result confirmed a short time later by Blackett and Occhialini.|| They are called positrons.

The Dirac equations for a positron may be obtained from those for an electron by a simple transformation. Suppose that, referring to the equations (10), the equations for an electron of positive mass are obtained by substituting $p_0 = (W/c) + (\epsilon V/c)$. The corresponding equations for an electron of negative mass will then be obtained by replacing W/c by $-W/c$. If we write in these equations $W^+ = W$, $p_1^+ = -p_1$, $p_2^+ = -p_2$, $p_3 = -p_3$, we obtain

$$\left(\frac{W^+}{c} - \frac{\epsilon V}{c} - mc\right)\psi_1 + (p_1^+ - ip_2^+)\psi_4 + p_3^+\psi_3 = 0,$$

$$\left(\frac{W^+}{c} - \frac{\epsilon V}{c} - mc\right)\psi_2 + (p_1^+ + ip_2^+)\psi_3 - p_3^+\psi_4 = 0,$$

$$\left(\frac{W^+}{c} - \frac{\epsilon V}{c} + mc\right)\psi_3 + (p_1^+ - ip_2^+)\psi_2 + p_3^+\psi_1 = 0,$$

$$\left(\frac{W^+}{c} - \frac{\epsilon V}{c} + mc\right)\psi_4 + (p_1^+ + ip_2^+)\psi_1 - p_3^+\psi_2 = 0.$$

† *Proc. Roy. Soc. A*, **133** (1931), 80.

§ *Ibid.* **41** (1932), 405; **43** (1933), 491.

‡ *Phys. Rev.* **35** (1930), 939.

|| *Proc. Roy. Soc. A*, **139** (1933), 699.

These are of exactly the same form as for an electron of positive mass and energy W^+ , except that the potential energy function is changed from $-\epsilon V/c$ to $+\epsilon V/c$ and the functions ψ_1, ψ_2 are interchanged with ψ_3, ψ_4 respectively. They correspond in fact to a particle with z -component of spin $\pm \frac{1}{2}\hbar$, of mass m , and charge $+\epsilon$.

The scattering of positrons by a static field of force as, for example, the Coulomb field of a bare atomic nucleus, may be treated in exactly the same way as that described in § 4 for electrons, the only difference being the change of sign of the potential energy. A positron, however, represents also a vacant electronic state and under certain conditions an electron may make a transition to this state, leading to the annihilation of both electron and positron. The inverse process in which an electron, in an unobservable state with negative mass, absorbs sufficient energy to raise it to an unoccupied level with positive mass, leads to apparent creation of a pair, e.g. an electron and positron, the positron being the manifestation of the vacant state of negative mass left by the transition. In calculating the probability of such transitions it is best to consider them as the transitions of an electron between electronic states, with the condition that the energy and momentum of the positron are equal and opposite to that of an electron in the state of negative mass.

Some further remarks about the creation and annihilation of electron-positron pairs are made in Chapter XV. We confine ourselves in this chapter to problems involving single particles only.

5.1. *The scattering of fast positrons by a Coulomb field*

The formula of § 4 may be applied to positrons by changing $Z\epsilon$ to $-Z\epsilon$. This makes no difference to the scattering to the approximation (42), but, when $Z/137$ is not small compared with unity, it introduces very considerable modifications. These have been worked out in detail by Massey† for scattering by mercury nuclei, using the calculations of Bartlett and Welton‡ for electrons as a basis. His results are illustrated in Fig. 12(b) in the form of the angular variation of the ratio r to the Rutherford scattering, for various values of v/c . These may be compared directly with the corresponding results for electrons and it will be seen that they are quite different. At present there are no experimental results available against which to check the theory.

† Ibid. A, 181 (1942), 14.

‡ Loc. cit., § 4.2.

COLLISIONS BETWEEN TWO PARTICLES: NON-RELATIVISTIC THEORY

1. Introduction

IN the first three chapters of this book we have discussed the motion of beams of electrons in various fields. If one assumes that the individual electrons of the beam do not interact with one another, the behaviour of the beam can be described by a wave function $\psi(x, y, z, t)$ in three-dimensional space, $|\psi|^2 dx dy dz$ giving the probability that an electron will be found, at time t , in the volume-element $dx dy dz$. When we wish to discuss atomic systems in which it is necessary to take into account the interaction between two or more particles, this is no longer possible; a wave function which is a function of the coordinates of all the particles must be used. Examples of problems for the solution of which a wave function of this type must be used are: the treatment of atoms containing more than one electron; the hydrogen atom, when the finite mass of the nucleus is taken into account; the scattering of α -particles by light nuclei for which the recoil of the nucleus cannot be neglected; an exact theory, including inelastic collisions, of scattering of electrons by atoms.

In this chapter we discuss first the problem of the interaction between two unlike particles (§ 2). In § 3 we give a brief discussion of the stationary states possible for atoms or molecules containing two similar particles, and in §§ 4 and 5 we discuss the collision between similar particles, with and without spin. It may be emphasized here that if the particles are unlike, it is not necessary to take account of the spin, unless their velocities are comparable with that of light, in which case a relativistic theory must be used (Chap. XV). If, however, the particles are similar, one must take account of the spin even in a non-relativistic theory.

2. Interaction of two unlike particles. Non-relativistic theory without spin

Let us suppose that the particles are an electron and a proton; our theory can then be applied to the problem of the hydrogen atom, and to the problem of the scattering of electrons by a hydrogen nucleus. As in the case of the one-body problem, the result of any experiment can be deduced from a wave function ψ . ψ will be a function of the

coordinates of both particles; if

$$\begin{aligned}\mathbf{r}_p &= (x_p, y_p, z_p) \\ \mathbf{r}_e &= (x_e, y_e, z_e)\end{aligned}$$

are the coordinates of the proton and of the electron respectively, the wave function will be of the form

$$\psi(\mathbf{r}_e, \mathbf{r}_p; t).$$

The interpretation of this wave function is as follows: if $d\tau_e$ and $d\tau_p$ are two elements of volume situated at the points \mathbf{r}_e and \mathbf{r}_p , then

$$|\psi(\mathbf{r}_p, \mathbf{r}_e; t)|^2 d\tau_p d\tau_e$$

is the probability that the proton is in the volume-element $d\tau_p$ and that the electron is in the volume-element $d\tau_e$, both at the instant of time t .

The wave function ψ satisfies Schrödinger's equation

$$-\frac{i\hbar}{2\pi} \frac{\partial \psi}{\partial t} = \frac{\hbar^2}{8\pi^2 m_p} \nabla_p^2 \psi + \frac{\hbar^2}{8\pi^2 m_e} \nabla_e^2 \psi - V(\mathbf{r}_p, \mathbf{r}_e) \psi. \quad (1)$$

Here

$$\nabla_p^2 = \frac{\partial^2}{\partial x_p^2} + \frac{\partial^2}{\partial y_p^2} + \frac{\partial^2}{\partial z_p^2}.$$

m_p , m_e are the masses of the proton and electron respectively; $V(\mathbf{r}_p, \mathbf{r}_e)$ denotes the potential energy of the pair of particles when the proton is at the point \mathbf{r}_p , and the electron at the point \mathbf{r}_e .

As an example, we shall obtain the solution which describes the motion of a hydrogen atom in field-free space. The potential energy function in this case is

$$V(\mathbf{r}_p, \mathbf{r}_e) = -\epsilon^2 / |\mathbf{r}_p - \mathbf{r}_e|.$$

As in the classical mechanics, the problem is separable; it is possible to discuss separately the motion of the centre of gravity, and of the line joining the particles. We make the substitution

$$\begin{aligned}(m_p + m_e)\mathbf{R} &= m_p \mathbf{r}_p + m_e \mathbf{r}_e \\ \mathbf{r} &= \mathbf{r}_p - \mathbf{r}_e,\end{aligned} \quad (2)$$

so that \mathbf{R} is the position of the centre of gravity of the two particles, and \mathbf{r} denotes the length and direction of the line joining them. The operator

$$\frac{\hbar^2}{8\pi^2 m_p} \nabla_p^2 + \frac{\hbar^2}{8\pi^2 m_e} \nabla_e^2$$

transforms into†

$$\frac{\hbar^2}{8\pi^2 M} \nabla_R^2 + \frac{\hbar^2}{8\pi^2 m^*} \nabla_r^2,$$

where $M = m_p + m_e$, $m^* = m_p m_e / (m_p + m_e)$.

† See, for instance, Sommerfeld, *Wave Mechanics*, p. 27, where this transformation is treated in detail.

The wave equation (1) becomes, therefore,

$$-\frac{i\hbar}{2\pi} \frac{\partial \psi}{\partial t} = \frac{\hbar^2}{8\pi^2 M} \nabla_{\mathbf{R}}^2 \psi + \frac{\hbar^2}{8\pi^2 m^*} \nabla_{\mathbf{r}}^2 \psi + \frac{\epsilon^2}{r} \psi. \quad (3)$$

This equation is separable; that is to say, we can obtain a solution of the form

$$f_0(\mathbf{r}, t)g_0(\mathbf{R}, t). \quad (4)$$

Substituting (4) in (3), we obtain the pair of equations

$$\begin{aligned} -\frac{i\hbar}{2\pi} \frac{\partial f_0}{\partial t} &= \frac{\hbar^2}{8\pi^2 m^*} \nabla^2 f_0 + \frac{\epsilon^2}{r} f_0 + A f_0 \\ -\frac{i\hbar}{2\pi} \frac{\partial g_0}{\partial t} &= \frac{\hbar^2}{8\pi^2 M} \nabla^2 g_0 - A g_0, \end{aligned}$$

where A is a constant. The substitution

$$f_0 = f \exp(+2\pi i A t / \hbar)$$

$$g_0 = g \exp(-2\pi i A t / \hbar)$$

leads to

$$-\frac{i\hbar}{2\pi} \frac{\partial f}{\partial t} = \frac{\hbar^2}{8\pi^2 m^*} \nabla^2 f + \frac{\epsilon^2}{r} f \quad (5)$$

$$-\frac{i\hbar}{2\pi} \frac{\partial g}{\partial t} = \frac{\hbar^2}{8\pi^2 M} \nabla^2 g, \quad (6)$$

and we may thus take ψ to be equal to fg , where f and g satisfy (5) and (6).

Equation (6) is the wave equation for a free particle of mass M ; the solution $g(\mathbf{R}, t)$ describes the behaviour of the centre of gravity of the atom. The particular solution required depends on the experiment which it is wished to discuss. If, for instance, ψ is the wave function describing a beam of atoms, g must be the wave function for a beam of particles, which was found in Chap. I, § 4. If the position and velocity of the atom are known approximately, with errors subject to the uncertainty principle, then g must have the form of the wave packet described in Chap. I, § 9.

Equation (5) is the wave equation for a particle of mass m^* and charge ϵ moving in the field of a fixed nucleus. If we wish to describe a hydrogen atom in its normal state, f must be the first characteristic solution of this equation.

3. Theory of the interaction between two similar particles

(This section is intended to be a summary of the usual theory of the stationary states of systems containing two similar particles.)

We shall suppose first that the particles have no spin. A particle with no spin has only three degrees of freedom,† its state being completely

† We do not wish to imply that the α -particle and carbon nucleus have 'really' only

determined when its position in space is given. [This is of course not true of an electron, because its magnetic moment can point in any direction.] The helium nucleus (i.e. the α -particle) and the carbon nucleus are examples of this kind of particle; the evidence that this is the case is discussed below.

Before considering collision phenomena we must remind ourselves of certain properties of the *stationary states* which are possible for molecules (He_2 , C_2H_2 , etc.) containing *two* such particles. If we wish to calculate the energy values which are possible for such a molecule, we proceed as follows: Let us take the case of the helium molecule He_2 . We first assign a coordinate to each particle, \mathbf{R}_1 , \mathbf{R}_2 for the two nuclei, and \mathbf{r}_1 , \mathbf{r}_2 , \mathbf{r}_3 , \mathbf{r}_4 for the electrons. We then write down the Schrödinger equation for the system; this is of the form

$$(H - E)\psi = 0, \quad (7)$$

where ψ is a function of the coordinates of the six particles, and H is the usual operator. As is well known, bounded solutions ψ can only be found for a certain series of values of E , the 'eigenvalues', which we denote by

$$E_0, E_1, E_2, \dots$$

We expect these to be the possible values of the energy of the molecule. Actually, only *half* the predicted number are found to occur in nature—i.e. in the band spectrum of the molecule.† We must now examine the reason for this fact.

Apart from accidental degeneracies, which can in general be removed by electric and magnetic fields, there corresponds, to each discrete eigenvalue E_n of the energy, a unique wave function

$$\psi_n(\mathbf{R}_1, \mathbf{R}_2; \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4),$$

which is a solution of the differential equation (7). These solutions all have the property that they are *either* symmetrical in the coordinates

three degrees of freedom—i.e. that they are not complex structures which can be split up into their component parts. We mean simply that in the experiments considered the probability of the internal structure of the nucleus being in any stationary state other than its normal state is negligible, and also that the normal state is non-degenerate; and thus, when the nucleus is at rest in free space, three coordinates are sufficient to specify its state.

In considering the collision between atoms moving with gas-kinetic velocities, or indeed with any energy less than the first resonance potential, the helium atom may be treated as a 'particle without spin' (cf. Chap. XII, § 3.1).

† Cf. Kronig, *Band Spectra*, p. 94. The statement is only true if it is understood to refer to a given electronic state, because some of the theoretically possible electronic states do not occur, owing to the exclusion principle.

$\mathbf{R}_1, \mathbf{R}_2$, or they are antisymmetrical; that is to say, either

$$\psi_n(\mathbf{R}_1, \mathbf{R}_2; \mathbf{r}_1 \dots) = \psi_n(\mathbf{R}_2, \mathbf{R}_1; \mathbf{r}_1 \dots) \quad (\text{symmetrical}),$$

or

$$\psi_n(\mathbf{R}_1, \mathbf{R}_2; \mathbf{r}_1 \dots) = -\psi_n(\mathbf{R}_2, \mathbf{R}_1; \mathbf{r}_1 \dots) \quad (\text{antisymmetrical}).$$

This property is not an assumption about the wave functions; it is a deduction from the differential equation that the wave functions satisfy. The proof† depends on the assumption that the mass and charge of the two particles are exactly the same, so that the operator H is symmetrical in the coordinates of the two particles.

It can further be deduced from the wave equation, that if the molecule is in a state described by a symmetrical wave function, then no possible disturbance can bring the molecule into a state described by an antisymmetrical wave function. The converse is also true. This is true not only of the *stationary* states; if a system containing the two nuclei is in any state described by a symmetrical wave function, the wave function will remain symmetrical under any perturbation whatever; and vice versa. The proof‡ depends essentially on the assumption that, given any field, and two points P and P' , the potential energy with the particles at rest at P and P' respectively does not depend on *which* particle is at P and *which* at P' . If the particles were very slightly different, in mass or in charge, then this would not be the case, and in general a perturbation (such as a collision) would give a finite, if small, probability for a transition from a symmetrical to an antisymmetrical state.

We have already seen that only half of the mathematically possible values of the energy of the molecule occur in nature. It is found, for the molecules C_2 and He_2 , that the energy values which occur are those for which the corresponding wave function is symmetrical in the coordinates of the nuclei. No reason is known at present why this should be so,§ and we must regard it simply as an experimental fact; it is, however, consistent with, but not demanded by, the laws of quantum mechanics that either only symmetrical or only antisymmetrical states should occur, because, as we have seen, these laws demand that a molecule that is once in a symmetrical state will never make a transition to an antisymmetrical state. The fact that only half the states are

† The proof is given at the end of this section.

‡ Cf. Dirac, *Quantum Mechanics*, 3rd edition, p. 208.

§ Unless we regard the α -particle and the carbon nucleus as complex systems formed from a given number of neutrons and protons; we can then deduce the symmetry properties of the nuclei from the corresponding properties of the neutron and proton.

observed, and that the missing states do not appear under any disturbance, shows that the properties of any two helium or carbon nuclei must be absolutely identical. It also proves that the particles have no fourth degree of freedom (spin)—at any rate in their normal state, since in fact they are complex particles.

We now pass on to the consideration of particles with spin, such as the electron, proton, and most nuclei. As we have seen in Chapter IV, such particles have a fourth coordinate s , the energy of the particle if passed into a magnetic field H along the z -axis being proportional to sH . For electrons and protons s can only have the values ± 1 ; for nuclei other than protons certain other values are allowed.† A particle with spin is thus specified by the coordinates (\mathbf{r}, s) . We shall denote this group of four coordinates by θ .

If we wish to calculate the energy-levels of a system containing two particles with spin, such as the helium atom, which contains two electrons, we are faced with the difficulty that the Hamiltonian for such a system is not known exactly,‡ the corrections introduced by the spin being of the same order of magnitude as the 'relativity corrections'. The assumption that this Hamiltonian exists leads, however, to important qualitative results in agreement with experiment about the number and order of magnitude of the energy-levels, and the possibility of transitions from one to another.

Let, then, H be the Hamiltonian of a system containing two similar particles with spin, let us say a helium atom. To find the energy-levels we must solve the wave equation

$$(H - E)\psi = 0.$$

There will as before be a series of energy-levels E_n for which bounded solutions can be obtained, and corresponding wave functions $\psi_n(\theta_1, \theta_2)$. The operator H must be symmetrical in the coordinates of the two particles; therefore, as before, the wave functions corresponding to every non-degenerate stationary state will be either symmetrical or antisymmetrical; that is to say, we shall have

$$\psi_n(\theta_1, \theta_2) = \pm \psi_n(\theta_2, \theta_1).$$

† In the usual theory of hyperfine structure a nucleus is assigned an angular momentum $i\hbar/2\pi$ ($i = 0, \frac{1}{2}, 1, \dots$), and a magnetic moment $ig(i)\epsilon\hbar/4\pi mc$, where $g(i)$ is a number of the order $1/1000$. The extra energy arising from the interaction with the magnetic field H due to the electronic shell is $m_H H g(i)\epsilon\hbar/4\pi mc$, where m_H is the component of i along H . Cf., for example, Pauling and Goudsmit, *Structure of Line Spectra* (1930), p. 202.

‡ Cf. Chap. XV.

As before, transitions between states of opposite symmetry cannot occur under any perturbation.

For all particles that have been investigated it is found that either only the energy-levels with antisymmetrical wave functions occur (electrons, protons) or only the energy-levels with symmetrical wave functions (α -particles, carbon or nitrogen nuclei). As we have seen already, this fact is consistent with wave mechanics, but not demanded by it.

The possibility of ascertaining whether a given energy-level observed experimentally has a symmetrical or antisymmetrical wave function, although we have no exact theory of the interaction of particles with spin, depends on the fact that the spin forces are small. We should expect the wave function describing any non-degenerate state of, say, the helium atom to be of the form, approximately,

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(s_1, s_2),$$

where ψ , to a very good approximation, is a solution of Schrödinger's equation for point electrons. To calculate the energy-levels of the atom one proceeds as follows. First one solves Schrödinger's equation for point electrons; the solutions are of course symmetrical or antisymmetrical in $\mathbf{r}_1, \mathbf{r}_2$. Both sets of energy-levels are found to occur; but the levels with antisymmetrical wave functions (orthohelium) are found on close resolution to be triplets. This is explained as being due to the spin; χ has four stationary states, three symmetrical, and one antisymmetrical; these are, to the zero-order approximation:

$$\begin{aligned} &\chi_\alpha(s_1)\chi_\alpha(s_2), && \chi_\beta(s_1)\chi_\beta(s_2), \\ &\chi_\alpha(s_1)\chi_\beta(s_2) \pm \chi_\alpha(s_2)\chi_\beta(s_1). \end{aligned}$$

For the definitions of χ_α, χ_β cf. Chap. IV, § 2. Thus, corresponding to every solution of Schrödinger's equation, there are four theoretically possible energy-levels; the fact that the observed parhelium-levels are singlets and the orthohelium-levels triplets shows that only wave functions occur which are antisymmetrical† in θ_1, θ_2 .

In the case of the homonuclear diatomic molecules the procedure is

† Particles for which only antisymmetrical wave functions can exist are said to satisfy the Fermi-Dirac statistics; particles for which only symmetrical wave functions can exist, the Einstein-Bose statistics. Particles which obey the Fermi-Dirac statistics obey also the 'exclusion principle', as can easily be shown. For if two such particles are in states described by wave functions ψ_a, ψ_b , then the wave function describing the pair of particles is

$$\psi_a(\theta_1)\psi_b(\theta_2) - \psi_a(\theta_2)\psi_b(\theta_1).$$

But if the two states are the same, this wave function vanishes; therefore the two particles cannot be in the same state.

essentially the same; we solve the Schrödinger equation, neglecting the spin of the nuclei. The splitting produced by the nuclear spin is too small to be observed directly; the spin multiplicity of a given state is revealed only through its statistical weight, which affects the relative intensity of certain of the rotational bands. (Cf. Kronig, *Band Spectra and Molecular Structure* (1930), pp. 94 et seq.; cf. also the article by Kallmann and Schuler, *Ergebnisse d. exakt. Naturwiss.* **11** (1932), 156.)

3.1. *Proof that the wave functions describing systems containing two similar particles in a non-degenerate stationary state are either symmetrical or antisymmetrical in the coordinates of the particles*

Let 1, 2 denote the coordinates of the particles; then $\psi(1, 2)$, the wave function, satisfies

$$H(1, 2)\psi(1, 2) - E\psi(1, 2) = 0, \quad (\alpha)$$

where H is some operator which is symmetrical in the coordinates of the particles. Since we assume that the state is non-degenerate, ψ is the only bounded solution of (α) .

Interchanging the coordinates 1 and 2 in (α) , we obtain

$$[H(2, 1) - E]\psi(2, 1) = 0. \quad (\beta)$$

But since H is symmetrical in the coordinates of the particles, $H(2, 1)$ is equal to $H(1, 2)$. Hence from (β) we obtain

$$[H(1, 2) - E]\psi(2, 1) = 0. \quad (\gamma)$$

It follows from (γ) that $\psi(2, 1)$ is a solution of equation (α) . But since $\psi(1, 2)$ is the only solution of (α) which is everywhere bounded, we must have

$$\psi(2, 1) = A\psi(1, 2),$$

where A is a constant. But it is clear that

$$\iint [\psi(1, 2)]^2 d\tau_1 d\tau_2 = \iint [\psi(2, 1)]^2 d\tau_1 d\tau_2,$$

and that neither integral is zero.

It follows that $A^2 = 1$.

Hence, since all the quantities in these equations are real, we have

$$A = \pm 1.$$

This is what we set out to prove. We must emphasize that the proof only applies to non-degenerate states. States with unquantized (positive) energy are always degenerate. For such states the theorem is not true.

Reference. For the general theory of non-combining states, see Dirac, *Principles of Quantum Mechanics*, 3rd edition, Chap. IX.

4. Collision of two identical particles without spin

We suppose first that the particles have no spin (α -particles). Imagine an experiment similar to that illustrated in Fig. 15. α -particles are fired with velocity v at a screen AB , and α -particles are also fired with equal and opposite velocity at a screen CD . Apertures in the screens are opened and shut again, not necessarily at the same moment. Wave packets would pass through. Let these have wave functions

$$u(\mathbf{r}, t), \quad v(\mathbf{r}, t)$$

both normalized to unity.† The problem before us is how to calculate the wave function at a time t after the collision. The simplest procedure would be to assign to the particles coordinates $\mathbf{r}_1, \mathbf{r}_2$, where \mathbf{r}_1 is the

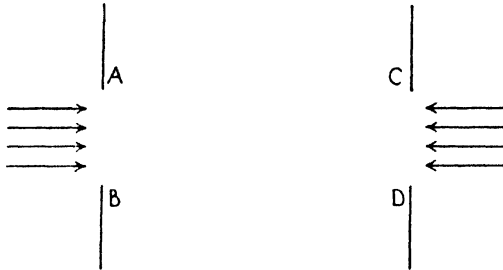


FIG. 15.

coordinate of the particle which passed through AB , etc. Thus the wave function before the collision would be

$$u(\mathbf{r}_1, t)v(\mathbf{r}_2, t), \tag{8}$$

and the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, t)$ after the collision would be determined by means of a wave equation of the type (1) and this initial condition. To interpret the wave function one would assume $|\psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d\tau_1 d\tau_2$ to be the probability of the first α -particle being in the volume-element‡ $(\mathbf{r}_1, d\tau_1)$ at time t and the second α -particle in the volume-element $(\mathbf{r}_2, d\tau_2)$. The probability of finding one or other of the particles at $(\mathbf{r}_1, d\tau_1)$ and the other at $(\mathbf{r}_2, d\tau_2)$ is thus (omitting t)

$$[|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2] d\tau_1 d\tau_2. \tag{9}$$

This method of treating the problem cannot, however, be correct. The reason for this is that if we take the initial wave function (8), and suppose there to be electrons present also, then we obtain a finite probability of a molecule being formed, and moreover a finite pro-

† i.e. such that $\int |u(\mathbf{r}, t)|^2 d\tau = 1$.

‡ We use the notation $(\mathbf{r}, d\tau)$ to denote a volume-element at the point \mathbf{r} , and of volume $d\tau$.

bability for the formation of *any* of the mathematically possible stationary states. Now this is contrary to experiment; we know that for He_2 only the stationary states with wave functions symmetrical in the coordinates of the nuclei are found in nature. We know also that if a wave function is initially symmetrical, it must remain symmetrical for all time. Thus we shall obtain agreement with experiment if we make our initial wave function symmetrical in the coordinates of the two α -particles.

The only way in which we can combine the wave packets u and v to form a symmetrical function is by taking for our initial wave function

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = k[u(\mathbf{r}_1)v(\mathbf{r}_2) + u(\mathbf{r}_2)v(\mathbf{r}_1)], \quad (10)$$

where k is some constant. We must consider now the interpretation of this wave function; the value that must be assigned to k will then become apparent.

Since initially the wave packets do not overlap, it follows that, for any value of \mathbf{r}_1 for which $u(\mathbf{r}_1)$ is finite, $v(\mathbf{r}_1)$ vanishes. Thus at time $t = 0$,

$$u(\mathbf{r}_1)v(\mathbf{r}_1) = 0.$$

Hence we have, when ψ is given by (10) above,

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = k^2|u(\mathbf{r}_1)v(\mathbf{r}_2)|^2 + k^2|u(\mathbf{r}_2)v(\mathbf{r}_1)|^2. \quad (11)$$

Now u is a function which vanishes except in the neighbourhood of the slit AB , and v vanishes except in the neighbourhood of CD . Thus $|\psi|^2$ vanishes unless \mathbf{r}_1 is near AB , and \mathbf{r}_2 near CD , or vice versa. Thus we cannot interpret $|\psi|^2 d\tau_1 d\tau_2$ as being the probability that the particle observed at AB is in the volume-element $(\mathbf{r}_1, d\tau_1)$, etc., because this latter probability is zero if \mathbf{r}_1 is near CD . We must interpret $|\psi|^2 d\tau_1 d\tau_2$ as the probability that one α -particle (either of the two) is in the volume-element $d\tau_1$, and the other in the volume $d\tau_2$. It is clear that (11) gives this probability correctly if we put k equal to unity.†

We adopt this interpretation, therefore, of *any* wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ describing two identical particles. We may note that if this interpretation is to make sense, $|\psi|^2$ must be symmetrical, i.e. we must have

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2.$$

There are *two* ways in which, at time $t = 0$, we can form a wave function with this property; the two possible wave functions are

$$u(\mathbf{r}_1)v(\mathbf{r}_2) \pm u(\mathbf{r}_2)v(\mathbf{r}_1).$$

† Note that this gives $\iint |\psi|^2 d\tau_2 d\tau_1 = 2$.

Wave functions for two identical particles ought therefore to be normalized to 2.

Thus we see that with the interpretation given above we *must* use either a symmetrical or an antisymmetrical wave function; if it were not that, for He_2 , no antisymmetrical states occur in nature, we should not know which to use, and it would be impossible to make predictions by means of wave mechanics, in collision problems of this type.

Of course it is not *a priori* necessary to interpret ψ in this way; we could use the unsymmetrical wave function, $u(\mathbf{r}_1)v(\mathbf{r}_2)$, at time $t = 0$, and make the interpretation that $|\psi|^2 d\tau_1 d\tau_2$ is the probability that a particular one of the two particles is at \mathbf{r}_1 . The objection to this course is, as we have emphasized, that it leads to finite probabilities for the formation of molecules in antisymmetrical stationary states, which are not observed.

The use of the symmetrical wave function will give different scattering probabilities from those obtained using unsymmetrical wave functions. If we use the latter, the initial wave function is $u(\mathbf{r}_1)v(\mathbf{r}_2)$; after time t let the wave function be $\psi(\mathbf{r}_1, \mathbf{r}_2, t)$. We have to make the interpretation that $|\psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d\tau_1 d\tau_2$ is the probability that the particle that was originally at AB is at $(\mathbf{r}_1, d\tau_1)$ and the other at $(\mathbf{r}_2, d\tau_2)$, while $|\psi(\mathbf{r}_2, \mathbf{r}_1, t)|^2 d\tau_1 d\tau_2$ is the probability that the particle which was originally at AB is in the volume $(\mathbf{r}_2, d\tau_2)$, etc. Thus the probability that one particle is at $(\mathbf{r}_1, d\tau_1)$ and the other at $(\mathbf{r}_2, d\tau_2)$ is (cf. equation (9))

$$\{|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2\} d\tau_1 d\tau_2. \quad (12)$$

On the other hand, if we use the symmetrical wave function, the initial wave function is

$$u(\mathbf{r}_1)v(\mathbf{r}_2) + u(\mathbf{r}_2)v(\mathbf{r}_1)$$

and the wave function after time t is

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t) + \psi(\mathbf{r}_2, \mathbf{r}_1, t), \quad (13)$$

and the probability that a particle is at $(\mathbf{r}_1, d\tau_1)$ and the other at $(\mathbf{r}_2, d\tau_2)$ is

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, t) + \psi(\mathbf{r}_2, \mathbf{r}_1, t)|^2 d\tau_1 d\tau_2, \quad (14)$$

i.e. $[\ |\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2 + \psi(\mathbf{r}_1, \mathbf{r}_2)\psi^*(\mathbf{r}_2, \mathbf{r}_1) +$

$$+ \psi(\mathbf{r}_2, \mathbf{r}_1)\psi^*(\mathbf{r}_1, \mathbf{r}_2)] d\tau_1 d\tau_2. \quad (15)$$

We have seen that the use of the symmetrical wave function (13) forbids us to assign a probability to the event of a particular α -particle being found in the volume $d\tau_1$ —let us say, the α -particle which was originally in the neighbourhood of AB . If an α -particle is observed at a given point, it is in general impossible, by any conceivable experiment, to find out whether it is the α -particle which was originally at AB , or the other. Thus the wave function give us no more information than can be obtained experimentally. It is only possible in principle to know

which α -particle is observed, if the path of the wave packet describing one α -particle does not overlap at any point with the path of the wave packet describing the other α -particle. It is in principle possible to devise such an experiment with slow α -particles ($8\pi\epsilon^2/hv \gg 1$). In Fig. 16 the shaded areas represent the paths of the two wave packets. It is clear that if a particle is observed at P it must be the one which was originally at AB . Hence it appears that in this case the symmetrical

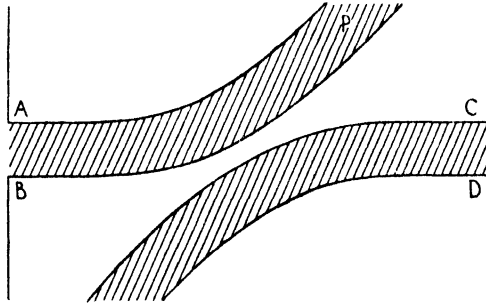


FIG. 16.

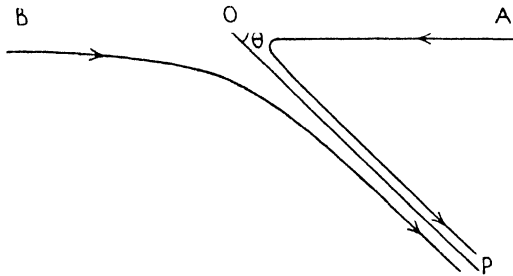


FIG. 17.

wave function gives us less information than could be obtained experimentally. However, here the unsymmetrical wave function will give us the same probabilities of finding a particle as the symmetrical wave function, because the 'cross term' $\psi(\mathbf{r}_1, \mathbf{r}_2)\psi^*(\mathbf{r}_2, \mathbf{r}_1)$ in (15) vanishes for all $\mathbf{r}_1, \mathbf{r}_2$.

We must now consider in greater detail how to calculate the scattering when two particles collide. For purposes of calculation it is simplest to consider steady beams of infinite width. We therefore consider two beams moving with equal and opposite velocities $\frac{1}{2}v$ parallel to the z -axis. We require to find the number of scattered particles that will be observed travelling in the direction OP making an angle θ with BA . The particle may have been deflected through an angle θ from BO , or an angle $\pi - \theta$ from AO , as shown in Fig. 17.

We introduce coordinates $\mathbf{r}_1, \mathbf{r}_2$ to describe the two particles; we then transform to

$$\begin{aligned}\mathbf{r} &= \mathbf{r}_1 - \mathbf{r}_2 \\ \mathbf{R} &= \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2).\end{aligned}$$

We find† that a wave function can be obtained of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R})\psi(\mathbf{r}).$$

In our case, since the centre of gravity is at rest, Ψ is a constant. ψ satisfies the equation

$$\nabla^2\psi + \frac{8\pi^2m^*}{\hbar^2}[\frac{1}{2}m^*v^2 - V(r)]\psi = 0, \quad (16)$$

where

$$m^* = \frac{1}{2}m$$

and $V(r)$ is the mutual potential energy of the particles. A solution $\psi(\mathbf{r})$ is obtained by the methods of Chapter II, having the form, for large r ,

$$\psi \sim e^{ikz} + f(\theta)r^{-1}e^{ikr},$$

where e^{ikz} represents‡ the 'incident wave' (in \mathbf{r} space), and $r^{-1}e^{ikr}$ the scattered wave. If the particles were distinguishable, one could use this wave function to describe the scattering; $|f(\theta)|^2$ would be proportional to the probability that the line joining the particles is deflected through an angle θ . Thus the number of particles scattered along OP would be proportional to

$$|f(\theta)|^2 + |f(\pi - \theta)|^2.$$

We must, however, use the symmetrical wave function

$$\psi(\mathbf{r}_1, \mathbf{r}_2) + \psi(\mathbf{r}_2, \mathbf{r}_1).$$

By interchanging \mathbf{r}_1 and \mathbf{r}_2 , \mathbf{r} is changed to $-\mathbf{r}$. r is therefore unaltered and θ is changed to $\pi - \theta$. The symmetrical wave function is therefore

$$e^{ikz} + e^{-ikz} + r^{-1}e^{ikr}[f(\theta) + f(\pi - \theta)]. \quad (17)$$

The incident wave may be written

$$2 \cos kz = 2 \cos k(z_1 - z_2);$$

the average value of $|\psi|^2$ for the incident wave is therefore 2, and so [cf. § 3, p. 97, footnote] the wave represents *one* particle per unit area in each beam. We deduce from (17) that the probability that a scattered particle will be found in a volume-element $d\tau_1$, and the particle with which it collided in the volume-element $d\tau_2$ is

$$\frac{1}{r^2} |f(\theta) + f(\pi - \theta)|^2 d\tau_1 d\tau_2,$$

† Cf. § 1 of this chapter.

‡ For the case of the Coulomb field the form of the incident wave is more complicated: cf. Chap. III, § 1.

where r is the distance between $d\tau_1$ and $d\tau_2$, and θ the angle that the line joining $d\tau_1$ and $d\tau_2$ makes with the z -axis.

It follows that the effective cross-section for a collision in which either particle is deflected into the solid angle $d\omega$ is

$$|f(\theta) + f(\pi - \theta)|^2 d\omega. \quad (18)$$

The probability of scattering when one of the particles is initially at rest is easily obtained. In a given collision the paths of the scattered particle and the knocked-on particle are at right angles. If an α -particle moving with velocity v strikes a stationary α -particle (He nucleus) the effective cross-section $I(\theta) d\omega$ for a collision in which a particle is scattered through an angle θ into a solid angle $d\omega$ is, from (18) (cf. Chap. VIII, § 10),

$$I(\theta) d\omega = |f(2\theta) + f(\pi - 2\theta)|^2 4 \cos \theta d\omega. \quad (19)$$

It is to be noted that (19) gives the probability that a particle will be observed moving in a direction making an angle θ with the direction of motion of the incident beam; the particle may be either a scattered α -particle from the incident beam, or a knocked-on helium nucleus. If a collision is observed, it is impossible to tell after the collision which is the incident particle and which the knocked-on particle, and, according to the wave mechanics, the question has no meaning.

4.1. Coulomb field

If the interaction between the particles may be represented with sufficient accuracy by the Coulomb field $V(r) = (Z\epsilon)^2/r$, then $f(\theta)$ is known, and is†

$$f(\theta) = \frac{Z^2\epsilon^2}{2m^*v^2} \operatorname{cosec}^2 \frac{1}{2}\theta \exp[i\alpha \log(1 - \cos \theta) + 2i\eta_0 + i\pi],$$

where $m^* = \frac{1}{2}m$, $\alpha = 2\pi(Z\epsilon)^2/hv$, and η_0 does not contain θ . From (19) we see that

$$I(\theta) = \left(\frac{Z^2\epsilon^2}{mv^2}\right)^2 [\operatorname{cosec}^4\theta + \sec^4\theta + 2\Phi \operatorname{cosec}^2\theta \sec^2\theta] 4 \cos \theta, \quad (20)$$

where $\Phi = \cos(\alpha \log \tan^2\theta)$.

The corresponding formula‡ according to the classical mechanics is obtained from (20) by putting Φ equal to zero.

It will be noticed that formula (20) predicts that at 45° twice as many particles will be scattered as are predicted by the classical theory.

The number scattered at a given angle according to formula (20) does

† Cf. equation (16) of this chapter, and Chap. III, § 1.

‡ Cf. Rutherford, Chadwick, and Ellis, p. 262.

not tend to the number to be expected according to the classical theory, as $v \rightarrow 0$. The scattering *between any two* angles does, however, tend to the classical value, owing to the rapid oscillation between $+1$ and -1 of the function Φ for varying θ , when v is small and hence α is large.

Formula (20) has been verified experimentally for the scattering of α -particles in helium.† Rather slow α -particles have to be used, because it is only then that the assumption of inverse square law forces between the nuclei is sufficient. Cf. Chap. XIII, § 2.35.

5. Collisions between two identical particles with spin

In the preceding section we have considered the collision between two similar particles which, firstly, have no spin, and, secondly, obey the Einstein-Bose statistics. In this section we consider the collision between particles, such as electrons and protons, which have spin—i.e. half a quantum of angular momentum, and obey the Fermi-Dirac statistics. The results may easily be generalized for particles with any number of quanta of angular momentum, and obeying either statistics, as is shown in § 6.

In the experiment considered at the beginning of the last section, if the particles have spin, the wave function which describes a particle must be a function of the spin coordinates. Let the particle which is passed through the slit AB have spin in the direction 1 , so that the wave function describing the particle is‡

$$u(\mathbf{r})\chi_l(s).$$

Similarly, let the wave function describing the other particle be

$$v(\mathbf{r})\chi_n(s).$$

Then since we must use an *antisymmetrical* wave function to describe the collision, the wave function at times before the collision is§

$$u(1)\chi_l(1)v(2)\chi_n(2) - u(2)\chi_l(2)v(1)\chi_n(1).$$

The wave function at a time after the collision, neglecting the small probability that the spins change their direction, is therefore

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \chi_l(1)\chi_n(2)\psi(1, 2) - \chi_l(2)\chi_n(1)\psi(2, 1). \quad (21)$$

The probability, therefore, that one particle is in the volume-element $(\mathbf{r}_1, d\tau_1)$ and the other in the volume-element $(\mathbf{r}_2, d\tau_2)$ is, at time t ,

$$\sum_{s_1} \sum_{s_2} |\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2)|^2. \quad (22)$$

† Chadwick, *Proc. Roy. Soc. A*, **128** (1930), 114; Blackett and Champion, *Proc. Roy. Soc. A*, **130** (1931), 380. ‡ Cf. Chap. IV, § 2, where definitions of χ_α , χ_β are given.

§ 1 stands for \mathbf{r}_1 or s_1 , 2 for \mathbf{r}_2 or s_2 .

Now, † if θ , ϕ be the polar angles of the direction \mathbf{l} , and θ' , ϕ' of \mathbf{n} , we have

$$\chi_l(s) = -\sin \frac{1}{2}\theta \chi_\alpha(s) + \cos \frac{1}{2}\theta e^{i\phi} \chi_\beta(s).$$

Hence

$$\sum_s |\chi_l(s)|^2 = 1,$$

and
$$\sum_s \chi_l(s) \chi_n^*(s) = \sin \frac{1}{2}\theta \sin \frac{1}{2}\theta' + \cos \frac{1}{2}\theta \cos \frac{1}{2}\theta' e^{i(\phi-\phi')}.$$

It follows that (22) is equal to

$$|\psi(1, 2)|^2 + |\psi(2, 1)|^2 - [\psi(2, 1)\psi^*(1, 2) + \psi(1, 2)\psi^*(2, 1)] \times \\ \times [\sin^2 \frac{1}{2}\theta \sin^2 \frac{1}{2}\theta' + \cos^2 \frac{1}{2}\theta \cos^2 \frac{1}{2}\theta' + 2 \cos \frac{1}{2}\theta \cos \frac{1}{2}\theta' \sin \frac{1}{2}\theta \sin \frac{1}{2}\theta' \cos(\phi - \phi')],$$

which reduces to

$$|\psi(1, 2)|^2 + |\psi(2, 1)|^2 - \frac{1}{2}[\psi(1, 2)\psi^*(2, 1) + \psi(2, 1)\psi^*(1, 2)](\cos \Theta + 1), \quad (23)$$

where Θ is the angle between the spin directions, namely,

$$\cos \Theta = \mathbf{l} \cdot \mathbf{n}.$$

Thus (23) may be written

$$A |\psi(1, 2) + \psi(2, 1)|^2 + B |\psi(1, 2) - \psi(2, 1)|^2,$$

where
$$A = \frac{1}{4}(1 - \cos \Theta), \quad B = \frac{1}{4}(3 + \cos \Theta).$$

Thus to obtain the probability of a given collision, one must calculate the probability using wave functions symmetrical in the space coordinates of the particles, and one must also calculate the probability using wave functions that are antisymmetrical. If the former probability is P_S and the latter P_A , then the actual probability is

$$\frac{1}{4}(1 - \cos \Theta)P_S + \frac{1}{4}(3 + \cos \Theta)P_A, \quad (24)$$

where Θ is the angle between the spins of the two colliding particles. If this angle is unknown—i.e. if the two colliding beams are unpolarized—we must average (24) for all Θ . Since the average value of $\cos \Theta$ is zero, the probability is

$$\frac{1}{4}[P_S + 3P_A]. \quad (25)$$

As an example, we shall suppose that a beam of electrons, of density such that one crosses unit area per unit time, collides with a single stationary free electron. It is required to calculate the probability, per unit time, that a collision takes place in which one of the particles, after the collision, moves in a direction lying in the solid angle $d\omega$ inclined at an angle θ to the direction of motion of the incident beam.

† Cf. Chap. IV, § 2.

$$\left. \begin{aligned} \text{Then} \dagger \quad P_S &= \frac{\epsilon^4}{m^2 v^4} [\operatorname{cosec}^4 \theta + \sec^4 \theta + 2\Phi \operatorname{cosec}^2 \theta \sec^2 \theta] 4 \cos \theta, \\ \text{and similarly,} \\ P_A &= \frac{\epsilon^4}{m^2 v^4} [\operatorname{cosec}^4 \theta + \sec^4 \theta - 2\Phi \operatorname{cosec}^2 \theta \sec^2 \theta] 4 \cos \theta, \end{aligned} \right\} \quad (26)$$

where
$$\Phi = \cos\left(\frac{2\pi\epsilon^2}{hv} \log \tan^2 \theta\right).$$

The actual probability is given by (24) or (25), according to whether or not the spin directions are known.

It will be noted that, if the spins are in the same direction, we must use the antisymmetrical solution only. A consequence is that no electrons will be scattered, or knocked on, through an angle of 45° . If, on the other hand, the spins are antiparallel, so that Θ is 180° , then the number scattered is

$$\frac{1}{2}[P_S + P_A],$$

which is equal to the number to be expected according to the classical theory.

In practice it is only possible to observe the scattering of a beam of electrons by stationary electrons when the 'stationary' electrons are bound in atoms. The incident beam must then have energy so great that the binding forces and motion of the atomic electrons may be neglected. If this is the case, we shall have

$$2\pi\epsilon^2/hv \ll 1.$$

The term Φ in (26) may therefore be replaced by unity, except at small angles, where the deviations from classical formulae are in any case small.

E. J. Williams[‡] has compared the formulae (25), (26) with experiment by counting forked tracks in a Wilson chamber, using electrons of energies 20,000 volts. Good agreement with the theoretical formula was obtained.

The scattering of protons by hydrogen has been investigated by Gerthsen,[§] and evidence in favour of the formula (25) obtained. Recent work of this kind has been concerned rather more with the determination of the short range non-Coulomb forces between two protons than with the effect of symmetry, but, in the analysis of the observations, this effect is allowed for. A discussion of this work is given in Chapter XIII, § 1.2.

[†] Cf. equation (20).

[‡] *Proc. Roy. Soc. A*, 128 (1930), 459.

[§] *Ann. d. Physik*, 9 (1931), 769.

6. Collisions between identical nuclei

If a beam of atoms is fired into a gas composed of the same kind of atom, and if the energy of the beam is such that the distance of closest approach for scattering at a given angle is less than the radius of the K ring, then the effect of the electrons on the collision may be neglected. The number of particles scattered will be given by the formula†

$$C_S P_S + C_A P_A.$$

where P_S , P_A are given by formulae (26), m and ϵ being equal to the mass and charge of the nuclei in question. C_S and C_A depend on the statistics obeyed by the nuclei, and also on the number of quanta of spin. The ratio $C_S:C_A$ is the same as the ratio of the intensities of the symmetrical to the antisymmetrical lines in the rotational band spectra of the diatomic molecule of the element concerned. Thus we should have

$$\begin{aligned} C_S:C_A &= s_n/(s_n+1) && \text{(Fermi-Dirac),} \\ &= (s_n+1)/s_n && \text{(Einstein-Bose),} \end{aligned}$$

where $s_n h/2\pi$ is the angular momentum of the nucleus ($s_n = \frac{1}{2}$ for protons, zero for He, 1 for N_{14} , etc.). For further information about nuclear spins the reader is referred to Bethe and Bacher, *Rev. Mod. Phys.* **8** (1937), 206.

† Cf., for example, Sexl, *Zeits. f. Physik*, **80** (1933), 559.

VI

INHOMOGENEOUS DIFFERENTIAL EQUATIONS

IN this chapter methods are given for the solution of certain differential equations of the type

$$L\Psi = F,$$

where L is a linear differential operator of the second order, and F is a known function.

1. Ordinary differential equations. The general solution

The general type of differential equation considered in this section is

$$\frac{d^2y}{dx^2} + 2p \frac{dy}{dx} + qy = f, \quad (1)$$

where p, q, f are known functions of x ; however, by means of the substitution

$$y = \Psi \exp\left[-\int p \, dx\right]$$

the equation may be reduced to the form

$$\frac{d^2\Psi}{dx^2} + Q\Psi = F. \quad (2)$$

We shall therefore confine our attention to the equation (2).

Note that if, in the equation

$$\frac{d^2y}{dx^2} + \frac{2}{x} \frac{dy}{dx} + qy = f, \quad (1.1)$$

one makes the substitution

$$y = x^{-1}\Psi,$$

one obtains

$$\frac{d^2\Psi}{dx^2} + q\Psi = fx. \quad (2.1)$$

There are several methods of obtaining a solution of (2).

Method I

We suppose that two independent solutions of the equation

$$\frac{d^2\psi}{dx^2} + Q\psi = 0 \quad (3)$$

are known. Let these solutions be ψ_1, ψ_2 . Then it follows from (3) that

$$\frac{d}{dx} \left(\psi_1 \frac{d\psi_2}{dx} - \psi_2 \frac{d\psi_1}{dx} \right) = 0.$$

We can therefore multiply ψ_1, ψ_2 by constants in such a way that

$$\frac{d\psi_1}{dx} \psi_2 - \frac{d\psi_2}{dx} \psi_1 = 1 \quad (\text{all } x). \quad (4)$$

If ψ_1, ψ_2 are chosen so that (4) is satisfied, then

$$\Psi = \psi_1(x) \int_a^x \psi_2 F dx + \psi_2(x) \int_x^b \psi_1 F dx \quad (5)$$

is a solution of (2), as may be verified by substituting (5) in the equation (2). Further, since (5) contains two arbitrary constants a and b , (5) is the general solution of (2).

This method is discussed further in Courant-Hilbert, *Methoden d. mathematischen Physik*, 1924, p. 273.

Method II

We suppose that one solution of equation (3) is known; denote this by ψ . Then if in equation (2) we make the substitution

$$\Psi = \psi \zeta,$$

we obtain

$$\frac{d^2 \zeta}{dx^2} \psi + 2 \frac{d\zeta}{dx} \frac{d\psi}{dx} = F.$$

It follows that

$$[\psi]^2 \frac{d\zeta}{dx} = \int_{\alpha}^x F \psi dx', \quad (6)$$

and hence that

$$\Psi = \psi(x) \int_{\beta}^x [\psi(x')]^{-2} dx' \int_{\alpha}^{x'} F(x'') \psi(x'') dx'', \quad (7)$$

which is the required solution, containing the two arbitrary constants α and β .

Method I is the most suitable for the problems considered in this chapter. A third method is given in § 2 for certain differential equations.

2. Solution satisfying boundary conditions

In this section we shall show how to find the solution of the equation

$$\frac{d^2 \Psi}{dx^2} + Q\Psi = F(x)$$

which satisfies certain boundary conditions. We shall take for Q and F functions satisfying the following conditions:

$$F(x) \rightarrow 0 \quad \text{as } x \rightarrow \infty;$$

$F(x)$ bounded and differentiable in the range $0 < x < \infty$, except at the point $x = 0$, where there may be a pole of order x^{-1} ;

$$Q(x) = A - U(x),$$

where A is a constant, and U a function such that

$$xU(x) \rightarrow 0 \quad \text{as } x \rightarrow \infty,$$

and $U(x)$ is bounded and differentiable, except at the point $x = 0$, where $U(x)$ may have a pole of the type $n(n+1)/x^2$ (n a positive integer or zero).

We shall impose on Ψ the two following boundary conditions:

(i) Ψ must be zero at the point $x = 0$. The indicial equation shows that one solution behaves like x^{n+1} and the other like x^{-n} near $x = 0$; there will thus be one solution which vanishes at the origin.

(ii) The second boundary condition depends on the sign of A . If A is positive, we set

$$A = k^2$$

and choose Ψ so that $\Psi \sim \text{const. } e^{ikx}$.

If A is negative we choose Ψ so that Ψ shall be bounded as $x \rightarrow \infty$. We shall see that these two conditions determine Ψ completely, and that it is always possible to find Ψ satisfying these two conditions, for all A except in one special case.

We discuss first the case when A is positive. The equation that we have to solve is

$$\frac{d^2\Psi}{dx^2} + [k^2 - U(x)]\Psi = F(x). \quad (8)$$

Let ψ_1 be the solution, which vanishes at the origin, of

$$\frac{d^2\psi}{dx^2} + [k^2 - U(x)]\psi = 0. \quad (9)$$

Let ψ_1 be so normalized that†

$$\psi_1 \sim \sin(kx + \eta) \quad (x \text{ large}).$$

Let ψ_2 be the solution of (9) such that

$$\psi_2 \sim k^{-1} \exp i(kx + \eta) \quad (x \text{ large}).$$

Then ψ_1 and ψ_2 satisfy, for all x ,

$$\psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} = 1,$$

and hence (5) is the general solution of (8). The solution which vanishes at the origin is clearly

$$\Psi = \psi_1(x) \int_a^x \psi_2 F dx - \psi_2(x) \int_0^x \psi_1 F dx. \quad (10)$$

Both integrals converge as $x \rightarrow \infty$; thus the solution with the required form for large x is obtained by putting $a = \infty$. The form for large x is

$$\Psi \sim -k^{-1} e^{ikx + i\eta} \int_0^\infty \psi_1 F dx. \quad (11)$$

† Cf. Chap. II, § 1.

Thus a solution of the required form can always be found, provided the integrals

$$\int_0^{\infty} F(x) \exp(\pm ikx) dx$$

converge.

We shall now discuss the case when A is negative. Putting

$$A = -\gamma^2$$

we have to solve the equation

$$\frac{d^2\Psi}{dx^2} + [-\gamma^2 - U(x)]\Psi = F(x), \quad (12)$$

subject to the conditions, Ψ zero at the origin and bounded at infinity.

As before, let ψ_1 be the solution of

$$\frac{d^2\psi}{dx^2} + [-\gamma^2 - U(x)]\psi = 0, \quad (13)$$

which vanishes at the origin. In general, this solution, suitably normalized, will behave for large x like $\exp(+\gamma x)$. It is only for certain series of values of γ (the eigenvalues) that ψ has the asymptotic form $\exp(-\gamma x)$.

If γ is not an eigenvalue, the required solution can be found as follows: Let ψ_2 be that solution of (13) which has asymptotic form

$$\psi_2 \sim \gamma^{-1} \exp(-\gamma x).$$

Then the required solution of (12) is

$$\Psi = \frac{1}{2} \left(\psi_1 \int_{\infty}^x \psi_2 F dx - \psi_2 \int_0^x \psi_1 F dx \right), \quad (14)$$

which tends to zero as x tends to infinity, if $F(x) \rightarrow 0$.

If γ is an eigenvalue, then the solution ψ_1 which vanishes at the origin has asymptotic form $\exp(-\gamma x)$; we must take for ψ_2 the solution which behaves like $\gamma^{-1} \exp \gamma x$; the solution of (12) which vanishes at the origin is

$$\Psi = \frac{1}{2} \left(\psi_1 \int_a^x \psi_2 F dx - \psi_2 \int_0^x \psi_1 F dx \right),$$

which for large x behaves like

$$\frac{1}{2} \left(e^{-\gamma x} \int_a^x \psi_2 F dx - e^{\gamma x} \gamma^{-1} \int_0^{\infty} \psi_1 F dx \right).$$

The first term may be shown to be bounded since $F \rightarrow 0$ as $x \rightarrow \infty$;

thus we can obtain a bounded solution if and only if

$$\int_0^x \psi_1 F dx \rightarrow 0. \quad (15)$$

A second method by which a solution of (12) may be obtained is that used in ordinary perturbation theory. We expand

$$F(x) = \sum_n a_n \psi_n(x), \quad (16)$$

$$\Psi(x) = \sum_n b_n \psi_n(x),$$

where the ψ_n are the normalized characteristic functions of the equation

$$\frac{d^2\psi_n}{dx^2} + [-\gamma_n^2 - U(x)]\psi_n = 0, \quad (17)$$

subject to the conditions that ψ should vanish at $x = 0$ and remain bounded at $x = \infty$.

The summation includes an integration over the continuous range of γ_n^2 ($-\gamma_n^2$ positive). There may not be any discrete values at all.

Substituting (16) into (12), multiplying by ψ_n , and integrating over all x , we obtain

$$b_n = a_n(\gamma_n^2 - \gamma^2)^{-1}.$$

If γ is one of the eigenvalues, say γ_m , then no solution vanishing at $x = 0$ and at $x = \infty$ exists unless $a_m = 0$; that is to say, unless

$$\int_0^\infty F(x)\psi_m(x) dx = 0,$$

which is the same condition as (15).

2.1. Integral equation for the phase

We consider the equation (12) of Chapter II,

$$\frac{d^2G}{dr^2} + \left[k^2 - U(r) - \frac{n(n+1)}{r^2} \right] G = 0. \quad (18)$$

For the scattering problem discussed in that chapter a proper solution G_p of this equation was required which had the asymptotic form

$$G_p \sim i^n(2n+1)k^{-1} \sin(kr - \frac{1}{2}n\pi) + ce^{ikr}. \quad (19)$$

It was shown that c is then given by

$$c = (2n+1)(e^{2i\eta_n} - 1)/(2ik),$$

where the proper solution had the asymptotic form

$$G_p \sim i^n(2n+1)k^{-1}e^{i\eta_n} \sin(kr - \frac{1}{2}n\pi + \eta_n).$$

If we rewrite (18) in the form

$$\frac{d^2G}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} \right] G = U(r)G,$$

then, from (11),

$$G_p \sim i^n(2n+1)k^{-1} \sin(kr - \frac{1}{2}n\pi) - k^{-1}e^{ikr - i\frac{1}{2}n\pi} \int_0^\infty \mathcal{G}U(r)G \, dr. \quad (20)$$

Here \mathcal{G} is the solution of the equation

$$\frac{d^2\mathcal{G}}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} \right] \mathcal{G} = 0,$$

which vanishes at the origin and has the asymptotic form $\sin(kr - \frac{1}{2}n\pi)$, i.e.

$$\mathcal{G} = \left(\frac{\pi r}{2k} \right)^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr).$$

Comparing (20) with (19) we have

$$\frac{1}{2i}(e^{2i\eta_n} - 1) = -e^{i\eta_n} \int_0^\infty \mathcal{G}U(r)G \, dr,$$

where $G(r) \sim \sin(kr - \frac{1}{2}n\pi + \eta_n)$. This gives the integral equation

$$\sin \eta_n = -\left(\frac{1}{2}\pi k \right)^{\frac{1}{2}} \int_0^\infty r^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr) U(r) G(r) \, dr.$$

This result is made use of in Chap. VII, § 6.3. The approximate formula (27) of Chapter II follows by replacing $G(r)$ by $\mathcal{G}(r)$ when $U(r)$ is small.

3. Partial differential equations

In this section we shall denote the position of a point in three-dimensional space by the Cartesian coordinates (x, y, z) , or by the spherical polar coordinates (r, θ, ϕ) , or by the vector \mathbf{r} .

We denote by L the operator

$$L = \nabla^2 + k^2 - U(r),$$

where $U(r)$ is a function such that

$$rU(r) \rightarrow 0 \quad \text{as } r \rightarrow \infty.$$

Let $F(x, y, z)$ be a function such that $rF \rightarrow 0$ as $r \rightarrow \infty$. It is our purpose in this section to find a solution ψ of the equation

$$L\psi = F(x, y, z) \quad (21)$$

satisfying the boundary conditions

ψ everywhere finite;

$$\psi \sim r^{-1}e^{ikr}f(\theta, \phi) \quad (\text{large } r); \quad (22)$$

where $f(\theta, \phi)$ is some function which we must find.

To solve (21) we expand ψ and F in series of spherical harmonics. Let

$$P_n^m(\cos \theta) = \sin^m \theta \frac{d^m}{d(\cos \theta)^m} P_n(\cos \theta) \quad (m \geq 0),$$

and let us use the convention that

$$P_n^m = P_n^{-m}.$$

We expand

$$F(x, y, z) = \sum_{n=0}^{\infty} \sum_{m=-n}^{m=+n} A_n^m(r) P_n^m(\cos \theta) e^{im\phi}.$$

Let the required solution ψ be

$$\psi(x, y, z) = \sum_n \sum_m B_n^m(r) P_n^m(\cos \theta) e^{im\phi}. \quad (23)$$

Substituting these expansions into (21), multiplying by

$$P_n^m(\cos \theta) e^{-im\phi} \sin \theta \, d\theta \, d\phi,$$

and integrating with respect to θ, ϕ over the surface of a sphere, we obtain

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dB_n^m}{dr} \right) + \left(k^2 - U(r) - \frac{n(n+1)}{r^2} \right) B_n^m = A_n^m(r). \quad (24)$$

Making the substitution $B_n^m = r^{-1} b_n^m$,

$$\text{we obtain} \quad \frac{d^2}{dr^2} b_n^m + \left(k^2 - U(r) - \frac{n(n+1)}{r^2} \right) b_n^m = r A_n^m(r),$$

which is an equation of the type considered in §§ 1 and 2. The solution of (24) with the required boundary conditions is therefore, from (14),

$$B_n^m = -k L_n(r) \int_r^{\infty} H_n(r) A_n^m(r) r^2 \, dr - k H_n(r) \int_0^r L_n(r) A_n^m(r) r^2 \, dr, \quad (25)$$

where L_n, H_n are solutions of the equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dL}{dr} \right) + \left(k^2 - U(r) - \frac{n(n+1)}{r^2} \right) L = 0,$$

L_n being the solution bounded at the origin and so normalized as to have asymptotic form †

$$L_n \sim (kr)^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n),$$

and H_n being the solution with asymptotic form

$$H_n \sim (kr)^{-1} \exp i(kr - \frac{1}{2}n\pi + \eta_n).$$

(23) and (25) give us the solution that we require.

† Cf. Chap. II, § 1. The condition that L shall be bounded at the origin defines η_n .

For many purposes it is useful to express the solution as a definite integral

$$\psi = \iiint K(\mathbf{r}, \mathbf{r}') F(x', y', z') dx' dy' dz'. \quad (26)$$

If we write for K

$$\begin{aligned} K &= -\frac{k}{4\pi} \sum_{n=0}^{\infty} (2n+1) L_n(r) H_n(r') P_n(\cos \Theta) \quad (r' > r), \\ &= -\frac{k}{4\pi} \sum_{n=0}^{\infty} (2n+1) H_n(r) L_n(r') P_n(\cos \Theta) \quad (r > r'), \end{aligned}$$

where $\cos \Theta = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi')$,

then it may easily be shown that (26) is the required solution. For†

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta P_n(\cos \Theta) P_n^m(\cos \theta) \exp(im\phi) = \frac{4\pi}{2n+1} P_n^m(\cos \theta') \exp(im\phi'). \quad (27)$$

It follows at once that (26) is the same as the solution given by (23) and (25).

3.1. Asymptotic form of the solution

For large r , and fixed \mathbf{r}' ,

$$K(\mathbf{r}, \mathbf{r}') \sim \frac{1}{4\pi} r^{-1} e^{ikr} \sum_{n=0}^{\infty} (2n+1) e^{-in\pi + i\eta_n} L_n(r') P_n(\cos \Theta).$$

If we denote by $\mathfrak{F}(r, \theta)$ the function‡

$$\mathfrak{F} = \sum_{n=0}^{\infty} (2n+1) i^n e^{i\eta_n} L_n(r) P_n(\cos \theta),$$

then $K(\mathbf{r}, \mathbf{r}') \sim -\frac{1}{4\pi} r^{-1} e^{ikr} \mathfrak{F}(r', \pi - \Theta)$.

The solution ψ therefore has asymptotic form

$$\psi \sim -\frac{1}{4\pi} r^{-1} e^{ikr} \iiint \mathfrak{F}(r', \pi - \Theta) F(x', y', z') dx' dy' dz', \quad (28)$$

provided that the integral converges.

The equation $L\psi = F(x, y, z)$, where

$$L = \nabla^2 - \gamma^2 - U(r)$$

can be solved in a similar way. A bounded solution can always be obtained unless γ is an eigenvalue of the equation (cf. § 2)

$$L\psi = 0.$$

† Whittaker and Watson, *Modern Analysis*, p. 328.

‡ Chap. II, eq. (16). The asymptotic form of \mathfrak{F} is

$$\exp(ikz) + r^{-1} f(\theta) \exp(ikr).$$

4. Solution of the equation

$$(\nabla^2 + k^2)\psi = F(x, y, z). \quad (29)$$

This is a special case of the equation considered in the last section, the function $U(r)$ being put equal to zero. In this case

$$\mathfrak{Y}(r, \theta) = \exp(ikz),$$

and therefore the *asymptotic form* of the solution ψ is, from (28),

$$\psi \sim -\frac{1}{4\pi} r^{-1} e^{ikr} \iiint \exp(-ik\mathbf{n} \cdot \mathbf{r}') F(x', y', z') dx' dy' dz', \quad (30)$$

where \mathbf{n} is a unit vector in the direction θ, ϕ , and so

$$\mathbf{n} \cdot \mathbf{r}' = r' [\cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi')].$$

The solution ψ is

$$\psi = \iiint K(\mathbf{r}, \mathbf{r}') F(x', y', z') dx' dy' dz',$$

with

$$K = -\frac{1}{4\pi} \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|},$$

as may be shown from equation (27), or directly as follows:

We make use of the theorem† that if f, g are any two bounded twice differentiable functions of x, y, z , and Ω any volume bounded by a closed surface Σ ,

$$\int_{\Sigma} \left(f \frac{\partial g}{\partial n} - g \frac{\partial f}{\partial n} \right) dS = \iiint_{\Omega} (f \nabla^2 g - g \nabla^2 f) dx dy dz. \quad (31)$$

Here $\partial/\partial n$ denotes differentiation normal to dS away from the volume Ω ; the surface integral on the left is to be taken over the surface Σ of Ω and the volume integral on the right throughout the volume of Ω . We apply this theorem by taking for f the solution ψ (assuming one to exist) of the equation (29) satisfying the boundary conditions. We take \mathbf{r}' for our independent variable, so that f is $\psi(\mathbf{r}')$. For g we take $K(\mathbf{r}, \mathbf{r}')$ considered as a function of \mathbf{r}' , \mathbf{r} being kept constant. For Ω we take the volume enclosed by two spheres ω_1, ω_2 , both with their centres at the fixed point \mathbf{r} . The radius of ω_1 is to be ρ_1 , and is finally to tend to infinity; the radius ρ_2 of ω_2 is finally to tend to zero. It will be seen that the point $\mathbf{r} = \mathbf{r}'$, at which K has a pole, is excluded from Ω .

We obtain

$$\int \left(\psi \frac{\partial K}{\partial n'} - K \frac{\partial \psi}{\partial n'} \right) dS' = \iiint (\psi \nabla^2 K - K \nabla^2 \psi) dx' dy' dz'. \quad (32)$$

† Jeans, *Electricity and Magnetism*, p. 160.

Now throughout Ω we have

$$\nabla^2 K = -k^2 K,$$

and

$$\nabla^2 \psi = -k^2 \psi + F(x', y', z').$$

Therefore the right-hand side of (32) is equal to

$$- \iiint K(\mathbf{r}, \mathbf{r}') F(x', y', z') dx' dy' dz'. \quad (33)$$

The integral on the left-hand side of equation (32) can be split up into two parts: the integral over the outer boundary ω_1 , and the integral over the inner boundary ω_2 . Using the asymptotic expressions for ψ , K , it is easily seen that the first integral tends to zero as the radius of ω_1 tends to infinity. The expression

$$\int_{\omega_2} K \frac{\partial \psi}{\partial n'} dS'$$

tends to zero as the radius of ω_2 tends to zero; since, however, K has a pole at the centre of the sphere, it follows that, as $\omega_2 \rightarrow 0$,

$$\begin{aligned} \int_{\omega_2} \frac{\partial K}{\partial n'} \psi dS' &\rightarrow -\psi(\mathbf{r}) \int_{\omega_2} \frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|^2} dS' \\ &\rightarrow -\psi(\mathbf{r}). \end{aligned}$$

Comparing this with (33), we have

$$\psi(\mathbf{r}) = \iiint K(\mathbf{r}, \mathbf{r}') F(x', y', z') dx' dy' dz',$$

which is what we set out to prove.

VII
 SCATTERING BY A CENTRE OF FORCE
 TREATMENT BY INTEGRAL EQUATION, AND
 MISCELLANEOUS THEOREMS

1. The Born approximation

OUR problem in this section is the same as that of Chapter II, namely, to calculate the scattering of a beam of particles by a field $V(r)$; we shall obtain an approximate formula which is only valid for fast particles, but which can be evaluated with much less labour than is required for the exact formula of Chap. II, eq. (17).

We have to solve the wave equation

$$\nabla^2\psi + [k^2 - U(r)]\psi = 0, \quad (1)$$

where $k^2 = 8\pi^2mE/h^2$, $U(r) = 8\pi^2mV(r)/h^2$,

and where ψ must have the asymptotic form

$$\psi \sim e^{ikz} + r^{-1}e^{ikr}f(\theta). \quad (2)$$

We make use of the theorem, proved in Chap. VI, § 4, that the most general bounded solution of the equation

$$\nabla^2\psi + k^2\psi = F(x, y, z),$$

where $F(x, y, z) = F(\mathbf{r})$ is a known function, is

$$\psi = G(x, y, z) - \frac{1}{4\pi} \int \frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} F(\mathbf{r}') d\tau',$$

where G is the general solution of

$$\nabla^2G + k^2G = 0.$$

It follows that the general solution ψ of (1) will satisfy the integral equation

$$\psi = G - \frac{1}{4\pi} \int \frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} U(r')\psi(\mathbf{r}') d\tau'. \quad (3)$$

The expression on the right of (3) represents an outgoing wave; thus, in order that ψ may have the asymptotic form (2), we must choose

$$G = e^{ikz}.$$

To obtain $f(\theta)$ we require the asymptotic form of (3) for large r . Denoting by \mathbf{n} a unit vector in the direction of \mathbf{r} , so that

$$\mathbf{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta),$$

we have $|\mathbf{r}-\mathbf{r}'| \sim r - \mathbf{n} \cdot \mathbf{r}' + \text{terms of order } 1/r$,

and hence from (3)

$$\psi \sim e^{ikz} - r^{-1} e^{ikr} \frac{1}{4\pi} \int e^{-ik\mathbf{n} \cdot \mathbf{r}'} U(r') \psi(\mathbf{r}') d\tau'. \quad (4)$$

Formulae (3) and (4) are exact. It is interesting to note that the scattered wave is that which would be produced if each element of volume scattered a wavelet of amplitude, at unit distance, $-2\pi m\hbar^{-2}V(r) d\tau$ times the amplitude of the wave at that point.†

We may obtain a formula for $f(\theta)$ if we assume that the wave is not much diffracted by the scattering centre. We may then replace $\psi(\mathbf{r}')$ in the integral in (4) by the unperturbed wave function $\exp(ikz')$. This approximation is only valid for fast particles (cf. § 2 and Chap. IX).

We then obtain from (2) and (4), dropping the dashes,

$$f(\theta) = -\frac{1}{4\pi} \int \exp[ik(\mathbf{n}_0 - \mathbf{n}) \cdot \mathbf{r}] U(r) d\tau, \quad (5)$$

where \mathbf{n}_0 is a unit vector along the z -axis, so that $z = \mathbf{n}_0 \cdot \mathbf{r}$. The integral may be evaluated by taking spherical polar coordinates α, β , the axis $\alpha = 0$ being taken in the direction of the vector $\mathbf{n}_0 - \mathbf{n}$. We obtain

$$f(\theta) = -\frac{1}{4\pi} \int_0^{2\pi} d\beta \int_0^\pi \sin \alpha d\alpha \int_0^\infty r^2 dr e^{iKr \cos \alpha} U(r),$$

where $K = k|\mathbf{n}_0 - \mathbf{n}| = 4\pi \sin \frac{1}{2}\theta/\lambda$, $\lambda = 2\pi/k = \hbar/mv$.

Carrying out the integrations over α, β , we obtain

$$f(\theta) = -\frac{8\pi^2 m}{\hbar^2} \int_0^\infty \frac{\sin Kr}{Kr} V(r) r^2 dr. \quad (6)$$

This is the required formula; the intensity scattered into the solid angle $d\omega$ is $|f(\theta)|^2 d\omega$.

If $V(r)$ is an atomic field, it is often convenient to transform (6) into an integral involving the charge density in the atom; if we denote by $-\epsilon\rho(r)$ the charge density at any point, we have

$$V(r) = -\frac{Ze^2}{r} + \epsilon^2 \int \frac{\rho(r') d\tau'}{|\mathbf{r} - \mathbf{r}'|}. \quad (7)$$

Using the formula‡

$$\int \frac{\exp(i\mathbf{n} \cdot \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\tau' = \frac{4\pi}{|\mathbf{n}|^2} e^{i(\mathbf{n} \cdot \mathbf{r})},$$

† Cf. Mott, *Proc. Roy. Soc. A*, **127** (1930), 658.

‡ Cf. Chap. XI, § 1.1.

we obtain, substituting (7) in (5),

$$\begin{aligned} f(\theta) &= \frac{8\pi^2 m}{\hbar^2} \epsilon^2 \frac{Z - F(\theta)}{K^2} \\ &= \frac{\epsilon^2}{2mv^2} [Z - F(\theta)] \operatorname{cosec}^2 \frac{1}{2}\theta, \end{aligned} \quad (8)$$

where

$$F(\theta) = 4\pi \int_0^\infty \rho(r) \frac{\sin Kr}{Kr} r^2 dr. \quad (9)$$

The quantity F is known as the atomic scattering factor, and has been tabulated over a certain range of K for all elements.†

The formula (8) may be compared with the corresponding formula for X-rays. The intensity of X-rays scattered by an atom through an angle θ into a solid angle $d\omega$ is‡

$$\left[\frac{\epsilon^2}{mc^2} F(\theta) \right]^2 d\omega (1 + \cos^2\theta).$$

A simple explanation may be given of the similarity between these two formulae.§

1.1. *Remarks about the scattering as given by the Born formula*

The scattered amplitude may be calculated either from formula (6) or (8). From either formula we see that the scattering is a function of $\sin \frac{1}{2}\theta/\lambda$ only, that is to say, of $v \sin \frac{1}{2}\theta$. This is not the case for the exact formula of Chapter II, and will therefore be true only under conditions (fast electrons) to which the Born formula can be applied.

It is clear from formula (6) that, if $V(r)$ tends to zero faster than r^{-3} as r tends to infinity, then $f(\theta)$ remains finite as θ tends to zero. This is true also of the exact formula (Chap. II, (17)) for $f(\theta)$.

For a given atom, the value of $f(\theta)$ for θ equal to zero is independent of v . $f(\theta)$ falls more steeply with increasing θ for large v than for small.

Since $F(\theta)$ tends to zero for increasing K , we see that for high velocities and large angles, $f(\theta)$ tends to $(Z\epsilon^2/2mv^2)\operatorname{cosec}^2 \frac{1}{2}\theta$, so that the scattering is mainly nuclear, as one would expect. The non-occurrence of the phase factor (Chap. III, eq. (16)) in $f(\theta)$ is a consequence of our use of the Born approximation.

† Cf. Chap. IX.

‡ Cf. Compton and Allison, *X-rays in Theory and Experiment*, p. 135, Chicago (1935).

§ Cf. Mott, loc. cit.

2. Connexion between the Born formula and the exact formula for $f(\theta)$

The exact formula for $f(\theta)$ is (cf. Chap. II, eq. (17))

$$f(\theta) = \frac{1}{2ik} \sum_{n=0}^{\infty} (2n+1)[\exp(2i\eta_n) - 1]P_n(\cos \theta). \tag{10}$$

The Born formula gives (cf. (6) above)

$$f(\theta) = -\frac{8\pi^2 m}{h^2} \int_0^{\infty} V(r) \frac{\sin Kr}{Kr} r^2 dr. \tag{11}$$

In this section we shall investigate under what circumstances the formula (11) is a good approximation to (10). In Chap. II, § 2, an approximate expression for η_n was found, valid for η_n small. The formula obtained was

$$\eta_n \simeq -\frac{8\pi^2 mk}{h^2} \int_0^{\infty} V(r)[f_n(r)]^2 r^2 dr, \tag{12}$$

where

$$f_n(r) = (\pi/2kr)^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr).$$

Since both (11) and (12) are obtained by treating $V(r)$ as a small perturbation, we should expect that, on substituting (12) in (10), we should obtain (11). That this is the case follows at once from the well-known expansion†

$$\frac{\sin Kr}{Kr} = \sum_n (2n+1)P_n(\cos \theta)[f_n(r)]^2,$$

if $\exp(2i\eta_n) - 1$ in (10) is replaced by $2i\eta_n$.

The formula (12) often gives good results for η_n even when η_n is comparable with $\frac{1}{2}\pi$; one cannot then use the Born formula, but (12) may be substituted directly in (10) (cf. Chap. IX, § 5).

3. Relativistic correction

So far we have ignored effects due to relativity. These may be taken into account by applying the method of Born's approximation to the Dirac equations.

The second-order equation for a component ψ_λ of the Dirac wave function may be written

$$\nabla^2 \psi_\lambda + \left[k^2 - \frac{2W}{\hbar^2 c^2} V(r) + \frac{V^2}{\hbar^2 c^2} - \frac{i}{\hbar c} \rho_1 \sigma \cdot \text{grad } V \right] \psi_\lambda = 0 \quad (\lambda = 1, 2, 3, 4),$$

† Watson, *Theory of Bessel Functions*, p. 363, eq. (3).

where W is the total energy, $k^2 = (W^2 - m^2c^4)/(\hbar^2c^2)$, and $\rho_1\sigma$ is the vector matrix, operating on λ , which has components

$$\rho_1\sigma_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad \rho_1\sigma_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix},$$

$$\rho_1\sigma_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}.$$

Following Born's approximation, in which the scattering potential is treated as small, we write

$$\nabla^2\psi_\lambda + k^2\psi_\lambda = \left[\frac{2W}{\hbar^2c^2}V(r) + \frac{i}{\hbar c}\rho_1\sigma \cdot \text{grad } V \right] a_\lambda e^{ikz},$$

the term V^2/\hbar^2c^2 being neglected. $a_\lambda e^{ikz}$ represents the component of the incident wave so, following (12) of Chapter IV, with $p_1 = p_2 = 0$, $p_3 = k\hbar$,

$$\frac{a_1}{a_3} = -\frac{k\hbar c}{W + mc^2} = -\frac{a_2}{a_4}.$$

We then find, as in (4),

$$\psi_\lambda \sim a_\lambda e^{ikz} + r^{-1}e^{ikr}u_\lambda(\theta, \phi),$$

where

$$u_3 = [\{\gamma - \frac{1}{2}(\gamma - 1)(1 - \cos \theta)\}a_3 + \frac{1}{2}(1 - \gamma)\sin \theta a_4]f(\theta),$$

$$u_4 = [\{\gamma - \frac{1}{2}(\gamma - 1)(1 - \cos \theta)\}a_4 - \frac{1}{2}(1 - \gamma)\sin \theta a_3]f(\theta),$$

$$f(\theta) = \frac{2\pi m}{\hbar^2} \int V(r')e^{ik(\mathbf{n}_0 - \mathbf{n}) \cdot \mathbf{r}'} d\tau',$$

$\mathbf{n}_0 \cdot \mathbf{n} = \cos \theta$, $\gamma = (1 - \beta^2)^{-\frac{1}{2}}$, $\beta = v/c$, v being the velocity of the particle.

The differential cross-section (see Chap. IV, § 4)

$$I(\theta) = \{|u_3|^2 + |u_4|^2\}/\{|a_3|^2 + |a_4|^2\}$$

$$= (1 - \beta^2 \sin^2 \frac{1}{2}\theta) |f(\theta)|^2 / (1 - \beta^2).$$

Comparing with (5, 6) it will be seen that the effect of relativity is to introduce the two factors, $(1 - \beta^2)^{-1}$ arising from Lorentz contraction and $1 - \beta^2 \sin^2 \frac{1}{2}\theta$ from the spin. Both of these are independent of the form of the scattering potential $V(r)$.

4. Classical limit of the quantum theory scattering formulae

It is well known that if one makes \hbar tend to zero in any formula of the quantum theory, one obtains the corresponding classical theory formula. It is interesting to show directly that this is so for our formula (Chap. II,

eq. (17)) for the number of particles scattered by a field $V(r)$. We can see also under what conditions the number of particles scattered is the same on both theories.

We require first an expression for the number of particles scattered, according to the classical theory.

If we take the scattering centre at the origin, then the equation of any orbit with energy E and angular momentum J is, in plane polar coordinates, r, ϕ ,

$$\phi + \int_{r_0}^r \frac{\partial}{\partial J} [2m(E-V) - J^2/r^2]^{\frac{1}{2}} dr = 0. \tag{13}$$

If r_0 be the positive zero of

$$2m(E-V) - J^2/r^2,$$

and if α be the angle between the asymptotes of the orbit, then

$$\frac{1}{2}\alpha = - \int_{r_0}^{\infty} \frac{\partial}{\partial J} [2m(E-V) - J^2/r^2]^{\frac{1}{2}} dr. \tag{14}$$

θ , the angle of deflexion, is given by the equation

$$\theta = \pi - \alpha. \tag{15}$$

Thus from (14) and (15) we know the momentum J corresponding to a given deflexion θ .

Suppose now that we have a stream of particles whose velocity is v and that N cross unit area per unit time. Then the probable number of particles that cross per unit time a plane perpendicular to the direction of flight, with angular momentum between J and $J+dJ$, is

$$2\pi NJ dJ/m^2v^2.$$

The number of particles deflected between angles θ and $\theta+d\theta$ is, therefore,

$$\frac{2\pi NJ dJ}{m^2v^2} \frac{dJ}{d\theta} d\theta,$$

J being given as a function of θ by (14) and (15). This number we have denoted by $2\pi NI(\theta)\sin\theta d\theta$ (cf. Chap. II, § 1). Thus we have

$$I(\theta) = \frac{J}{m^2v^2} \frac{dJ}{d\theta} \frac{1}{\sin\theta}. \tag{16}$$

We now consider the quantum-theory formula. We require the solution of

$$\frac{d^2L}{dr^2} + F(r)L = 0, \tag{17}$$

where
$$F(r) = \frac{8\pi^2m}{h^2} (E-V) - \frac{n(n+1)}{r^2}.$$

Since we are investigating the case when $\hbar \rightarrow 0$, we may suppose that F is large. With this assumption, the solutions of (17) are approximately†

$$F^{-\frac{1}{2}} \exp \left[\pm i \int^r F^{\frac{1}{2}} dr \right]. \quad (18)$$

We require the combination of these solutions that is finite at the origin. To find this, we note that $F(r)$ has a single zero, r_0 say, between $r = 0$ and $r = \infty$. $F(r)$ is negative for r less than r_0 , positive for r greater than r_0 . The solution (18) will therefore be oscillating for $r > r_0$, exponential for $r < r_0$. The solution that we require will clearly be the one that, for decreasing r , *decreases* exponentially as r becomes less than r_0 . This solution is, to the same approximation as‡ (18),

$$L_n(r) \simeq F^{-\frac{1}{2}} \sin \left[\frac{1}{4}\pi + \int_{r_0}^r F^{\frac{1}{2}} dr \right]. \quad (19)$$

(19) is a valid approximation to $L_n(r)$ only in the range $r > r_0$. For large r , the asymptotic form of (19) is

$$\text{const.} \times \sin \left[\frac{1}{4}\pi + \int_{r_0}^{\infty} \{F^{\frac{1}{2}} - k\} dr + k(r - r_0) \right],$$

where

$$k^2 = 8\pi^2 m E / \hbar^2.$$

For the expression η_n (Chap. II, eq. (15)) therefore, we have, to the desired approximation,

$$\eta_n = \frac{1}{4}\pi + \frac{1}{2}n\pi - kr_0 + \int_{r_0}^{\infty} [F^{\frac{1}{2}} - k] dr. \quad (20)$$

This expression for η_n may be used for the calculation of the quantum-theory scattering in cases where η_n is large (cf. § 6.2).

To obtain the scattered amplitude $f(\theta)$ we now have to sum the series (Chap. II, eq. (17)),

$$f(\theta) = \frac{1}{2ik} \sum (2n+1) [\exp(2i\eta_n) - 1] P_n(\cos \theta). \quad (21)$$

Since the greatest part of the value of the series is contributed by large values of n , we replace $P_n(\cos \theta)$ by its asymptotic form§ for large n

$$P_n(\cos \theta) \sim \left[\frac{2}{n\pi \sin \theta} \right]^{\frac{1}{2}} \sin \left[\left(n + \frac{1}{2} \right) \theta + \frac{1}{4}\pi \right].$$

† Jeffreys, *Proc. Lond. Math. Soc.*, Ser. 2, 23, Part 6, or Chap. I, § 6, of this book.

‡ Cf. Jeffreys, loc. cit. See also § 6.2 of this chapter.

§ See, for example, Jahnke-Emde, *Funktionentafeln*, p. 81.

We note first that the series

$$\sum_n (2n+1)P_n(\cos \theta) \quad (\theta \neq 0),$$

though divergent, is summable as the limit of a power series on its radius of convergence, and that the sum is zero. We may therefore subtract this series from (21). For $f(\theta)$ we obtain, therefore, the divergent but summable series

$$f(\theta) = \sum A(n)\{\exp[iB(n)] - \exp[iB'(n)]\}, \tag{22}$$

where

$$A(n) = -\frac{1}{2k} (2n/\pi \sin \theta)^{\frac{1}{2}},$$

$$B(n) = 2\eta_n + (n + \frac{1}{2})\theta + \frac{1}{4}\pi,$$

$$B'(n) = 2\eta_n - (n + \frac{1}{2})\theta - \frac{1}{4}\pi.$$

To sum such a series as

$$\sum_n A(n)\exp[iB(n)] \tag{23}$$

we inquire whether there is any value of n for which

$$\frac{dB(n)}{dn} = 0.$$

If there is any such value, n_0 say, then in the neighbourhood of n_0 there will be a large number of terms of the series over which $\exp[iB(n)]$ is not oscillating. Thus effectively all of the sum of the series comes from this region. (23) may then be replaced by

$$A(n_0)\exp[iB(n_0)] \int_{-\infty}^{+\infty} \exp\{i\beta(n-n_0)^2\} dn,$$

where

$$\beta = \frac{1}{2} \left(\frac{d^2 B}{dn^2} \right)_{n=n_0}.$$

Evaluating the integral, we obtain

$$A(n_0)(\pi/i\beta)^{\frac{1}{2}} \exp[iB(n_0)]. \tag{24}$$

We now inquire whether the differential coefficient of $B(n)$ or $B'(n)$ does in fact vanish for any positive value of n . The condition is

$$2 \frac{\partial}{\partial n} \int_{n_0}^{\infty} [F^{\frac{1}{2}} - k] dr + \pi \pm \theta = 0$$

for B and B' respectively. Putting

$$nh/2\pi = J,$$

this condition reduces to

$$\int_{r_0}^{\infty} \frac{\partial}{\partial J} [2m(E-V) - J^2/r^2]^{\frac{1}{2}} dr + \frac{1}{2}\pi \pm \frac{1}{2}\theta = 0. \quad (25)$$

If we take the negative sign we obtain equation (14), giving the classical angular momentum J of an electron scattered through an angle θ . One can easily see that if one takes the positive sign there is no positive J satisfying the equation. Thus in (22) the sum of the second series is much greater than the sum of the first, and we have for $f(\theta)$

$$f(\theta) = - \sum_n A(n) \exp[iB'(n)],$$

which reduces, by (24), to

$$-A(n_0)(\pi/i\beta)^{\frac{1}{2}} \exp[iB'(n_0)],$$

where $hn_0/2\pi$ is the root of (25). For β we have

$$\frac{\hbar}{2\pi} \frac{\partial^2}{\partial J^2} \int_{r_0}^{\infty} [2m(E-V) - J^2/r^2]^{\frac{1}{2}} dr,$$

which reduces by (25) to $\frac{\hbar}{4\pi} \frac{\partial \theta}{\partial J}$.

Putting in the value for $A(n_0)$ we obtain

$$|f(\theta)|^2 = J \frac{\partial J}{\partial \theta} / m^2 v^2 \sin \theta,$$

which is the classical formula for $I(\theta)$.

We see that the condition for classical scattering at a given angle θ is that n_0 should be large, where n_0 is the value of n for which

$$\frac{\partial \eta_n}{\partial n} = \frac{1}{2}\theta,$$

and that η_n should also be large for this value. Compare the condition of validity of Born's formula, which is that η_n shall be small for all n .

5. The range of validity of the Born and classical approximations

It is apparent that the two approximations considered in this chapter are largely complementary.

Broadly speaking, the classical approximation is valid, except at very small angles of scattering, when a large number of phases, many of which are large, are required to represent the scattering. On the other hand, the Born approximation holds when the phases are all small, and is less accurate at large than at small angles. Neither are valid when

the scattering is given in terms of a small number of phases some of which are large. Under these circumstances the exact treatment described in Chapter II is necessary.

To put this on a more definite basis, † let us consider first the scattering of a particle of mass m and velocity v by a field confined to a region of extension a in which its potential is of the order D . For a classical treatment to hold, two conditions must be satisfied:

- (a) the orbit of the particle must be well defined in relation to the distance;
- (b) the deflexion due to the collision must also be well defined.

The first requires that $mva \gg \hbar$, (26)

i.e. that the wave-length should be small compared with the dimensions of the scatterer. This corresponds to the condition in § 4 that the value of n , for which $\partial\eta_n/\partial n = \frac{1}{2}\theta$, should be large.

The second requires that, if Δp is the momentum transfer in the collision,

$$a\Delta p \gg \hbar.$$

Now Δp is of the order D/v so we must have

$$Da/\hbar v \gg 1. \tag{27}$$

This corresponds to the condition in § 4, that the value of η_n , for which $\partial\eta_n/\partial n = \frac{1}{2}\theta$, should be large.

Born's approximation will be valid, on the other hand, if

$$Da/\hbar v \ll 1, \tag{28}$$

no matter what the wave-length of the particle. ‡

When the conditions are such that neither (26) and (27), nor (29) hold the exact method must be used.

For scattering by a field, of potential $V(r)$, which falls off gradually with distance, the above considerations may be applied to the scattering through a particular angle θ . In the classical approximation this arises from that part of the field at a distance a from the origin where $V(a)/mv^2$ is of order θ . In order that the approximation should be valid for such scattering, we must have $a \gg \hbar/mv$ and $V(a) \gg \hbar v/a$. In terms of the angle θ the second condition can be written $a \gg \hbar/mv\theta$. Thus the two conditions are normally satisfied if $a\theta \gg \hbar/mv$.

On the other hand, in Born's approximation, the part of the field

† The following discussion is based on the article by E. J. Williams, *Rev. Mod. Phys.* 17 (1945), 217.

‡ This condition may be obtained from the considerations of § 2. It expresses the requirement that the value of η_0 given by (12) for the case considered should be $\ll 1$.

responsible for the scattering occurs at a distance of order $\hbar/mv\theta$ from the origin and the approximation is valid if $V(\hbar/mv\theta) \ll mv^2\theta$. (See Chap. IX, § 5, for a discussion of the validity of Born's approximation as applied to electron scattering by atoms.)

If we take the scattering by a Coulomb field, for which $V = Z\epsilon^2/r$, we have $V(a) \simeq mv^2\theta$ when $a = Z\epsilon^2/mv^2\theta$; so, for classical scattering, $Z\epsilon^2/mv^2\theta \gg \hbar/mv\theta$, i.e. $Z\epsilon^2/\hbar v \gg 1$. Similarly, for the Born approximation to be valid, $Z\epsilon^2mv\theta/\hbar \ll mv^2\theta$, i.e. $Z\epsilon^2/\hbar v \ll 1$. In this case either approximation is valid over the whole angular range or not at all. It is also a peculiarity that both approximations give the same answer, which is also the exact one. If, however, the Coulomb potential fails to hold outside a given distance a , say, the effect will become apparent at a different angle of scattering according to which approximation is valid. With the classical approximation it will occur when θ is of the order $Z\epsilon^2/mv^2a$, whereas with the Born approximation it will occur when θ is of the order \hbar/mva . This becomes important in the discussion of multiple scattering (see Chap. IX, § 6; Chap. XII, § 2.4) and of the stopping of fast particles (see Chap. XI, § 4.4, and Chap. XII, §§ 2.1, 2.3).

6. Summary of methods available for calculating the scattering by a central field

We have stated in the preceding section the conditions under which the Born and classical approximations are valid. When neither is available the complete expression,

$$I(\theta) = \frac{1}{4k^2} \left| \sum (2n+1)(e^{2i\eta_n} - 1)P_n(\cos\theta) \right|^2,$$

derived in Chapter II, must be used; but in many cases it is still possible to evaluate the phases η_n by approximate methods. These we shall now discuss, concluding with a brief summary of the method of numerical integration which must be resorted to when no other method of sufficient accuracy is available.

6.1. Approximation when the phase shift is small

This has been derived in Chap. II, eq. (27). It is a good approximation only when the phase shift is very small (usually 0.1 radian or less). This occurs either when the velocity is very large or, for $n > 0$, when it is very small. In the former case it is usually unnecessary to proceed by the method of partial cross-sections, Born's approximation being valid. For the latter case it was shown in § 2 that η_n is very small when a particle with angular momentum $\{n(n+1)\}^{1/2}\hbar$ would not penetrate the

atom (according to classical theory), i.e. if

$$V(r) \ll \frac{n(n+1)}{r^2} \frac{\hbar^2}{2m},$$

for r given by

$$kr \sim \{n(n+1)\}^{\frac{1}{2}}. \quad (29)$$

For values of n satisfying this condition the formula (27) of Chapter II is satisfactory.

6.2. Approximation when the phase shift is not small

A useful approximation in this case is to use the formula (20) of § 4, either in the form given there or in the equivalent form

$$\eta_n = \int_0^{\infty} \left\{ k^2 - \frac{2m}{\hbar^2} V - \frac{n(n+1)}{r^2} \right\}^{\frac{1}{2}} dr - \int_0^{\infty} \left\{ k^2 - \frac{n(n+1)}{r^2} \right\}^{\frac{1}{2}} dr, \quad (30)$$

where the lower limit of the integral in each case is the zero of the integrand.

The approximation is best when the potential is large and does not vary much in a wave-length. Langer† has given reasons why it may be improved by the substitution of $(n+\frac{1}{2})^2$ for $n(n+1)$. In particular this gives an approximation to η_0 for an attractive potential, a case for which (30) breaks down owing to the absence of a zero of the integrand.

Although it is not possible to formulate a condition as definite as (29) for the applicability of these approximations,‡ experience has shown that (30) may be used to give good results for phases as low as 0.2 radian. It has also confirmed the superiority of Langer's modification. Reference to results obtained with its use are given in Chap. X, § 4.

Care must be exercised in using the approximation when more than one zero of the function $k^2 - \frac{2m}{\hbar^2} V - \frac{n(n+1)}{r^2}$ exists. Provided that the amplitude of the wave in the inner regions, in which the function is positive, remains small compared with the amplitude in the outermost such region, then it is a good approximation to use (30) with the lower limit of the first integration given by the outermost zero. In certain

† *Phys. Rev.* 51 (1937), 669. The solution required is, strictly, not the one which decreases as r decreases from the zero of $k^2 - \frac{2m}{\hbar^2} V - \frac{n(n+1)}{r^2}$, but the one which vanishes at $r = 0$. Langer obtained this solution by substituting in the equation (17), $r = \log \rho$, $Lr^{-1} = G$. This gives for G an equation of the same form as (17) but with ρ in place of r and with $n(n+1)/r^2$ replaced by $(n+\frac{1}{2})^2/r^2$. Since $\rho \rightarrow -\infty$ as $r \rightarrow 0$ it is the solution of this new equation which decreases exponentially as ρ decreases from the appropriate zero ρ_0 , which is required. This gives the same result as (30) for η_n but with $(n+\frac{1}{2})^2$ in place of $n(n+1)$.

‡ See, however, H. and B. Jeffreys, *Methods of Mathematical Physics*, p. 490, Cambridge, 1946.

narrow ranges of values of k , however, the amplitude in the inner attractive regions may build up to relatively large values by a resonance effect. It is then impossible to neglect the contribution to the phase from these regions. The method may be extended to cover such cases by considering the connexion formulae for the approximate functions at each zero.

6.3. Variational method

Hulthén† has recently introduced a method for approximate determination of phases which is analogous to the variational method for approximate determination of proper energy values.

Consider
$$I = \int_0^{\infty} GDG \, dr, \quad (31)$$

where
$$D \equiv \frac{d^2}{dr^2} + k^2 - U(r) - \frac{n(n+1)}{r^2}.$$

If $rU(r) \rightarrow 0$ as $r \rightarrow \infty$, and G is a proper function satisfying the usual boundary conditions

$$G(0) = 0, \quad G \sim \sin(kr - \frac{1}{2}n\pi + \eta_n), \quad (32)$$

then the integral I exists. Furthermore, if G is the exact solution of the equation

$$\frac{d^2G}{dr^2} + \left\{ k^2 - U(r) - \frac{n(n+1)}{r^2} \right\} G = 0, \quad (33)$$

satisfying the condition (32), the integral vanishes.

Suppose now we substitute, instead of the exact solution, a function $G + \delta G$ which differs very slightly from G and is a proper function satisfying the boundary conditions (32), but with η_n replaced by $\eta_n + \delta\eta_n$. We have then

$$\delta G = 0, \quad r = 0,$$

$$\delta G \sim \cos(kr - \frac{1}{2}n\pi + \eta_n) \delta\eta_n.$$

Substituting in (31) we find

$$\delta I \equiv \int_0^{\infty} \delta GDG \, dr + \int_0^{\infty} GD(\delta G) \, dr.$$

The second integral may be transformed by partial integration, for

$$\begin{aligned} \int_0^{\infty} G \frac{d^2}{dr^2} (\delta G) \, dr &= \int_0^{\infty} \delta G \frac{d^2G}{dr^2} \, dr + \left[G \frac{d}{dr} (\delta G) - \delta G \frac{dG}{dr} \right]_0^{\infty} \\ &= \int_0^{\infty} \delta G \frac{d^2G}{dr^2} \, dr - k\delta\eta_n. \end{aligned}$$

† *Kungl. Fysio. Sällskapets Lund Förhand.* 14 (1944), 1.

We therefore have

$$\delta I = 2 \int_0^{\infty} \delta G D G \, dr - k \delta \eta_n = -k \delta \eta_n,$$

as G satisfies (33).

Thus, if G is varied in such a way that $I = 0$ for every δG , then $\delta I = 0$ and hence $\delta \eta_n = 0$. Unlike the case of discrete levels, however, η_n is, in general, neither a maximum nor a minimum.

To use the stationary property to obtain an approximate value ζ for η_n and an approximation $F(r)$ for G , the following procedure may now be adopted. A trial function $F(r; c_1, c_2, \dots, c_s)$ is chosen which is a proper function over the whole range of r , satisfies the boundary condition (32) at $r = 0$, and contains s undetermined parameters c_1, c_2, \dots, c_s besides the phase parameter ζ . This function is substituted for G in the integral I and the $s+1$ parameters determined from the equations

$$\begin{aligned} I(\zeta; c_1, c_2, \dots, c_s) &= 0, \\ \frac{\partial I}{\partial c_\nu} &= 0, \quad \nu = 1, \dots, s. \end{aligned}$$

As a check on the accuracy of the approximation, use may be made of the fact that, if G is the exact solution of (33) satisfying (32), then

$$\sin \eta_n = -(\frac{1}{2}\pi k)^{\frac{1}{2}} \int_0^{\infty} r^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr) U(r) G(r) \, dr,$$

a result proved in Chap. VI, § 2.1. If the function F is a good approximation, then

$$-(\frac{1}{2}\pi k)^{\frac{1}{2}} \operatorname{cosec} \zeta \int_0^{\infty} r^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr) U(r) F(r) \, dr$$

should be nearly equal to 1.

This method has been applied by Hulthén† to calculate η_n for potentials $V(r)$ of the form $Ar^{-1}e^{-br}$ for which it proves very satisfactory.

6.4. Numerical solution of the differential equation for G

The approximate methods are an advantage when a large number of phases are required and the accuracy aimed at is not too high. For more accurate work the variation method given above may provide the best procedure if an approximate analytical expression for the wave functions is also required.‡ In many cases it is best to proceed with direct numerical solution of the equations for the particular values of k and n concerned. With proper setting out of the work this can be carried out expeditiously. The following procedure, § similar to that used by Hartree in solving similar equations arising in his self-consistent field method, is a very convenient one.

† Loc. cit.

‡ For further alternative methods see Pais, *Proc. Camb. Phil. Soc.* **42** (1946), 45; Ramsey, *Proc. Camb. Phil. Soc.* **44** (1948), 87; and Ferretti and Krook, *Proc. Phys. Soc.* **60** (1948), 481.

§ We are indebted to Dr. R. A. Buckingham for contributing the description below.

We require the solution of the equation

$$\frac{d^2y}{dx^2} = -\left\{k^2 - v(x) - \frac{n(n+1)}{x^2}\right\}y, \tag{34}$$

$$= g(x)y,$$

for a sequence of values x_0, x_1, x_2, \dots , of x at a suitable constant interval h , satisfying prescribed conditions at x_0 .

We write
$$F = 4lh^3g(x)y, \tag{35}$$

where l is a constant chosen to suit the computation. From corresponding values of y and F we can form tables of differences, as shown below in Sheppard's central difference notation:

x_0	F_0	$\delta F_{\frac{1}{2}}$	$\delta^2 F_1$	$\delta^2 y_1$	$\delta y_{\frac{1}{2}}$	y_0
x_1	F_1	$\delta F_{\frac{1}{2}}$	$\delta^2 F_1$	$\delta^2 y_1$	$\delta y_{\frac{1}{2}}$	y_1
x_2	F_2	$\delta F_{\frac{1}{2}}$	$\delta^2 F_2$	$\delta^2 y_2$	$\delta y_{\frac{1}{2}}$	y_2
x_3	F_3	$\delta F_{\frac{1}{2}}$	$\delta^2 F_2$	$\delta^2 y_2$	$\delta y_{\frac{1}{2}}$	y_3

As a preliminary to the forward integration, a series expression for y in powers of $x-x_0$ must be found, consistent with the initial conditions at x_0 (e.g. by the method of Frobenius, or Taylor's series). This is used to give the values of y , F , and differences shown in heavy type. Subsequent values of y are found by the following cyclical process:

(i) Calculate $\delta^2 y_2$ using the equation

$$\delta^2 y_2 = \frac{1}{4l}\{F_2 + \frac{1}{12}\delta^2 F_2 - \frac{1}{240}\delta^4 F_2 + \dots\}, \tag{36}$$

with estimated values of $\delta^2 F_2$ and $\delta^4 F_2$. (It is advantageous to choose the interval h small enough for the $\delta^4 F$ term to be negligible; also l can be varied to suit any particular stage of the computation, although most often it is conveniently taken as unity.)

(ii) With this value of $\delta^2 y_2$, build up $\delta y_{\frac{1}{2}}$ and y_3 .

(iii) Calculate F_3 , using equation (35), form its differences, and verify that the new value of $\delta^2 F_3$ does not alter $\delta^2 y_2$; otherwise, make the necessary revision.

(iv) Compute y_4, F_4 , etc., by a similar cycle.

A regular check on the forward integration is provided by the approximate relation

$$\delta^4 y_r = \frac{1}{4l}\{\delta^2 F_r + \frac{1}{12}\delta^4 F_r\}. \tag{37}$$

This requires the higher differences $\delta^4 y_r$ and $\delta^4 F_r$ to be tabulated, in itself a valuable check on the rest of the work. The computed value of $\delta^4 y_r$ should not normally differ from the right-hand side of (37) by more than one unit in the last digit. Provided the discrepancies alternate in sign, one can then be fairly confident that the integration is proceeding without serious error.

When y assumes an oscillatory form, the interval h can be adjusted at convenient stages in the calculation to keep the values of $\delta^2 y$ at a reasonable size. For accuracy to 3 or 4 figures in y , however, not less than 8-10 intervals should be kept in each half-oscillation.

An alternative method of integration is that of Gauss-Jackson,† which uses the relation

$$y_r = \frac{1}{4l} \{ \delta^{-2} F_r + \frac{1}{2} F_r - \frac{1}{240} \delta^2 F_r + \dots \}, \tag{38}$$

where $\delta^{-2} F$ denotes the second sum of the function F , in place of (36). The scheme of differences is as follows:

x_0	$\delta^{-2} F_0$	F_0	y_0
	$\delta^{-1} F_{\frac{1}{2}}$	F_1	y_1
x_1	$\delta^{-2} F_1$	F_2	y_2
	$\delta^{-1} F_{\frac{3}{2}}$	F_3	y_3
x_2	$\delta^{-2} F_2$	F_4	y_4
	$\delta^{-1} F_{\frac{5}{2}}$	F_5	y_5
x_3	$\delta^{-2} F_3$	F_6	y_6

In this method only y_0 and y_1 need to be prescribed initially; then F_0 and F_1 are determined by (35), and $\delta^{-2} F_0$ and $\delta^{-2} F_1$ by equation (38), assuming that h is small enough for the $\delta^2 F$ term to be negligible. Thus all the quantities in heavy type are determined, and we proceed with the forward integration as follows:

(i) Estimate F_2 , or rather $\frac{1}{2} F_2$, and compute y_2 from equation (38).

(ii) Use this y_2 to find F_2 by equation (35); verify that the estimate of y_2 is not thereby affected, or if it is, make the necessary revision.

(iii) From F_2 build up $\delta^{-1} F_{\frac{3}{2}}$ and $\delta^{-2} F_3$, and thence proceed to estimate y_3 .

This is a somewhat simpler method than the previous one, and lends itself to even greater precision, as by suitable choice of l accumulation of rounding-off errors in the summation can be kept negligible. For this purpose either $l = 2.5$ or 5 is convenient in practice. A suitable overall check is provided by equation (36), which is applied in analogous fashion to (37) in the previous method.

To evaluate the phase angle the forward integration is continued until the further effect of the scattering potential is considered negligible. At such values of x , y can be written

$$y = A \{ \cos \eta_n j_{n+\frac{1}{2}}(kx) + (-1)^n \sin \eta_n j_{n-\frac{1}{2}}(kx) \}, \tag{39}$$

where $j_s(kx) = (\pi x/2k)^{\frac{1}{2}} J_s(kx)$. η_n may then be determined by smooth connexion of the integrated solution to (39) for large x .

† J. Jackson, *Mon. Note R. Ast. Soc.* **84** (1924), 602-6.

VIII

GENERAL THEORY OF ATOMIC COLLISIONS

IN Chapters II and III we discussed the scattering of a stream of particles by a centre of force. The great majority of collision phenomena, however, involve some reaction of the scattered particle on the scatterer. We shall now develop a more general theory applicable to such problems as the following:

- (1) The excitation of atoms and molecules by electron impact.
- (2) The excitation of vibration and rotation of molecules by the impact of other molecules.
- (3) The transfer of excitation between two atoms or molecules on collision.
- (4) The excitation of atomic nuclei by bombarding nuclei.

In all these cases there is a direct energy interchange between the relative translational motion and the internal motion of the colliding systems. There is no transfer of *particles* between the colliding systems on impact; this, however, occurs in a number of other types of collision which are of equal importance. These 'rearrangement' collisions include the following:

- (1) The capture of electrons from atoms by positively charged particles.
- (2) Emission of particles from atomic nuclei, with resultant capture of the incident nucleus.
- (3) Collisions of two molecules, resulting in a redistribution of electrons and nuclei.
- (4) Collisions of electrons with atoms, in which exchange of particles takes place between the incident beam and the scattering atom, the incident electron being captured and the atomic electron ejected.

Since one cannot distinguish experimentally between the scattered and ejected electrons, and since, moreover, the wave function used must be antisymmetrical in the coordinates of these two, this type of problem requires a somewhat different treatment to the other three. The particular case of the collision of two similar particles, which may be reduced to a one-body problem, has already been considered in Chapter V.

In what follows, we shall distinguish the two types of collision by the terms 'direct' and 'rearrangement' inelastic collision.

Owing to the complexity of the phenomena, it is necessary, except in very special cases, to use approximate methods of treatment. For collisions in which the relative velocity of the colliding systems is large compared with the velocities of their internal motion, there is no difficulty in obtaining an accurate approximation ('Born's approximation'); but under other circumstances no general method has yet been developed, and special methods must be used for particular problems. However, certain conservation theorems may be derived which are valid under general conditions. These may be used to place limits on the size of the cross-sections and to provide a check on results obtained by approximate methods.

1. Conservation theorems.† Maximum cross-sections for given angular momentum

We consider a stream of particles of mass m and velocity v incident on a scattering centre, as in Chapter II, but we now suppose that the particles may undergo inelastic, as well as elastic, collisions with the centre.

As in Chapter II we resolve the incident wave into partial waves of angular momentum $\hbar\{n(n+1)\}^{\frac{1}{2}}$. At large distances r from the centre the radial function representing the incident partial wave of order n will then be

$$(kr)^{-1}i^n(2n+1)\sin(kr - \frac{1}{2}n\pi),$$

where $k = mv/\hbar$. Corresponding to this there will be an elastically scattered partial wave of asymptotic form

$$r^{-1}c_n e^{ikr}.$$

The partial elastic cross-section Q_{el}^n will then be given by

$$Q_{el}^n = \frac{4\pi}{2n+1} |c_n|^2. \quad (1)$$

If only elastic scattering can occur, then there can be no net radial flux of particles, with given angular momentum and the initial energy, towards the scattering centre. When inelastic collisions can also occur, the net inward flux will be equal to the flux of particles which have suffered inelastic collisions. At a great distance r from the centre the net inward flux will therefore be given by

$$r^{-2} \frac{(2n+1)}{4\pi} Q_{in}^n, \quad (2)$$

where Q_{in}^n is the partial cross-section for inelastic collisions.

† Mott, *Proc. Roy. Soc. A*, **133** (1931), 228; Bohr, Peierls, and Placzek (we are indebted to Professor Peierls for making this work available to us in advance of publication).

The net inward radial flux of particles possessing the initial energy is given at a large distance r by

$$\frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial r} - \psi \frac{\partial \psi^*}{\partial r} \right),$$

where
$$\psi = r^{-1} \left[\frac{i^n}{k} (2n+1) \sin(kr - \frac{1}{2}n\pi) + c_n e^{ikr} \right], \quad (3)$$

and is therefore

$$\frac{-\hbar}{mr^2} \left[-\frac{1}{2}i(2n+1)(c_n^* - c_n) + k|c_n|^2 \right]. \quad (4)$$

It is easily verified that this flux vanishes when

$$c_n = (2n+1)(e^{2i\eta_n} - 1)/2ik, \quad (5)$$

η_n being a real phase. When this is so the elastic scattering may be represented in terms of real phase angles η_n , following the formulae (17) and (18) of Chapter II, even when the interaction with the scatterer cannot be represented by a potential $V(r)$.† On the other hand, if inelastic collisions can occur, this representation is no longer exact though, if the chance of such a collision is small, it will remain a good approximation.

The existence of inelastic collisions can be taken into account by allowing the phase η_n in the expression (5) to become complex. Thus, writing

$$\eta_n = \lambda_n + i\mu_n,$$

we have

$$Q_{\text{el}}^n = \frac{2\pi}{k^2} (2n+1) e^{-2\mu_n} \{ \cosh 2\mu_n - \cos 2\lambda_n \}, \quad (6)$$

$$Q_{\text{in}}^n = \frac{2\pi}{k^2} (2n+1) e^{-2\mu_n} \sinh 2\mu_n. \quad (7)$$

Equating (2) and (4) and using (1) gives

$$Q_{\text{tot}}^n = Q_{\text{in}}^n + Q_{\text{el}}^n = \frac{2\pi i}{k} (c_n^* - c_n),$$

where Q_{tot}^n is the partial cross-section for all collisions, both elastic and inelastic.

Since

$$|c_n|^2 \geq \left| \frac{c_n^* - c_n}{2} \right|^2,$$

$$Q_{\text{el}}^n = \frac{4\pi}{2n+1} |c_n|^2 \geq (Q_{\text{tot}}^n)^2 / Q_{\text{max}}^n,$$

where

$$Q_{\text{max}}^n = \frac{4\pi}{k^2} (2n+1).$$

† See, for example, Chap. X, § 5; Chap. XIII, §§ 1.1, 1.2, 1.3.

Hence, as

$$Q_{\text{el}}^n \not\approx Q_{\text{tot}}^n,$$

$$Q_{\text{tot}}^n \leq \frac{4\pi}{k^2}(2n+1), \quad (8)$$

the equality only arising when there is no inelastic scattering.

Further

$$Q_{\text{in}}^n = Q_{\text{tot}}^n - Q_{\text{el}}^n,$$

$$\leq Q_{\text{tot}}^n - (Q_{\text{tot}}^n)^2/Q_{\text{max}}^n.$$

The maximum value of the right-hand side occurs when

$$Q_{\text{tot}}^n = \frac{1}{2}Q_{\text{max}}^n,$$

so

$$Q_{\text{in}}^n \leq \frac{\pi}{k^2}(2n+1). \quad (9)$$

In this case, the equality only arises when Q_{el}^n is also equal to

$$\pi(2n+1)/k^2.$$

These formulae are especially useful in limiting cross-sections which can occur under resonance conditions of one sort or another. They only apply to partial cross-sections, no general rules being available for the total cross-section. However, if the range of the scattering field is small compared to the wave-length, only the zero-order partial wave is scattered and we then have

$$Q_{\text{tot}} \leq \frac{4\pi}{k^2}, \quad Q_{\text{in}} \leq \frac{\pi}{k^2}.$$

When the range R of the scattering field is well defined, it is also possible to obtain some useful limits when the wave-length is very short compared with R . The partial cross-sections for which

$$n \lesssim kR$$

will alone be important. Then

$$Q_{\text{tot}} = \sum_0^{kR} Q_{\text{tot}}^n, \quad Q_{\text{el}} = \sum_0^{kR} Q_{\text{el}}^n,$$

and

$$(Q_{\text{tot}})^2 \leq Q_{\text{el}} \sum_0^{kR} Q_{\text{max}}^n$$

$$\leq 4\pi R^2 Q_{\text{el}}.$$

This gives, in the same way as (8) and (9),

$$Q_{\text{tot}} \leq 4\pi R^2,$$

$$Q_{\text{in}} \leq \pi R^2, \quad (10)$$

the equality holding in the latter case only when Q_{el} is also equal to πR^2 .

This last result seems paradoxical if one considers the scatterer to be an inelastic sphere of radius R . For this case the inelastic cross-section

is clearly πR^2 . It is not so obvious how the equal elastic cross-section arises. The explanation is exactly the same as for the problem of the elastic scattering by a rigid sphere discussed in Chap. II, § 5. It was shown there that, for such a sphere, the total elastic cross-section for short wave-lengths is not πR^2 but $2\pi R^2$, the doubling being due to shadow diffraction which leads to elastic scattering concentrated within a cone of angle $1/kR$ about the direction of incidence. This effect arises also in the present case.

It is important to notice, for certain future applications, that the above arguments apply to collisions in which the incident particle can be absorbed by the scattering centre.

2. The collisions of electrons with hydrogen atoms. Born's approximation

In order to make clear the method which must be employed in dealing with inelastic collisions, we will first consider the simplest type of collision which occurs in practice, that of electrons with hydrogen atoms. The mass of the electron is small compared with that of the proton, and the motion of the latter in the collision can be neglected.

We consider a beam of electrons falling on a hydrogen atom initially in the normal state. The intensity of the beam is such that one electron crosses unit area per unit time. We have to find the number of electrons that are scattered per unit time through an angle θ into a solid angle $d\omega$ after having excited the atom into its n th state. This number, $I_n(\theta) d\omega$, has the dimensions of an area and will be called the differential cross-section for scattering into the solid angle $d\omega$. The total cross-section Q_n corresponding to the excitation will be obtained by integrating over all angles, so that

$$Q_n = \int_0^{2\pi} \int_0^\pi I_n(\theta) \sin \theta \, d\theta d\phi. \quad (11)$$

The wave equation for the system of incident electron and atom is

$$\left[\frac{\hbar^2}{8\pi^2 m} (\nabla_1^2 + \nabla_2^2) + E + \frac{\epsilon^2}{r_1} + \frac{\epsilon^2}{r_2} - \frac{\epsilon^2}{r_{12}} \right] \Psi = 0, \quad (12)$$

where the incident electron is distinguished by the suffix 1, the atomic electron by the suffix 2. The energy E is the sum of the energy E_0 of the atomic electron in its ground state and of the kinetic energy $\frac{1}{2}mv^2$ of the incident electron.

We may expand the function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \left(\sum_n + \int \right) \psi_n(\mathbf{r}_2) F_n(\mathbf{r}_1), \quad (13)$$

where the functions $\psi_n(\mathbf{r})$ are the proper functions for the hydrogen atom, satisfying

$$\left(\frac{\hbar^2}{8\pi^2m} \nabla^2 + E_n + \frac{\epsilon^2}{r} \right) \psi_n = 0. \quad (14)$$

The integral sign denotes integration over the functions of the continuous spectrum.

Substituting (13) in (12) and using (14), we obtain

$$\left(\sum_n + \int \right) \psi_n(\mathbf{r}_2) \left\{ \frac{\hbar^2}{8\pi^2m} \nabla^2 + E - E_n \right\} F_n(\mathbf{r}_1) = \left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_1} \right) \Psi'(\mathbf{r}_1, \mathbf{r}_2). \quad (15)$$

Multiplying both sides of this equation by $\psi_n^*(\mathbf{r}_2)$ and integrating over the coordinate space of the atomic electron, we obtain

$$\left\{ \frac{\hbar^2}{8\pi^2m} \nabla^2 + E - E_n \right\} F_n(\mathbf{r}_1) = \int \left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_1} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) \psi_n^*(\mathbf{r}_2) d\tau_2. \quad (16)$$

For large r_1 the right-hand side vanishes, and F_n satisfies the wave equation

$$\left\{ \nabla^2 + \frac{8\pi^2m}{\hbar^2} (E - E_n) \right\} F_n = 0, \quad (17)$$

which is the wave equation for a free particle of energy $E - E_n$. The associated wave-length is $2\pi/k_n$, where

$$k_n^2 = 8\pi^2m(E - E_n)/\hbar^2. \quad (18)$$

We notice that this wave-length is only real if $E > E_n$, i.e. if the electron has enough energy to excite the n th state of the atom. In this section we consider values of n for which this is the case.

Since the conditions of the problem require the electron to be incident on an atom in its normal state, the function $F_0(\mathbf{r}_1)$ must represent the sum of an incident and scattered wave; thus, F_0 must have the asymptotic form

$$F_0 \sim e^{ik_0z} + r^{-1} e^{ik_0r} f_0(\theta, \phi). \quad (19)$$

The functions F_n must represent scattered waves only, and so have asymptotic form

$$F_n \sim r^{-1} e^{ik_n r} f_n(\theta, \phi). \quad (20)$$

From (20) we deduce that $r^{-2} |f_n(\theta, \phi)|^2$ is the number of electrons per unit volume at distance r from the atom, which have excited the state n . Of these, the number crossing unit area per unit time is proportional to $k_n r^{-2} |f_n|^2$, whereas in the incident beam the number crossing unit area per unit time is proportional to k_0 . Hence we have (cf. Chap. II, § 1)

$$I_n(\theta) d\omega = \frac{k_n}{k_0} |f_n(\theta, \phi)|^2 d\omega. \quad (21)$$

The calculation of the asymptotic form of the functions $F_n(\mathbf{r}_1)$ cannot

be carried out exactly. For high velocities of impact, however, we may readily obtain approximate formulæ by a method due to Born.† Under these circumstances the perturbation of the incident wave by its interaction with the atom will be small.‡ We take, then, as zero-order approximation for Ψ , simply

$$\Psi = \exp(ik_0 \mathbf{n}_0 \cdot \mathbf{r}_1) \psi_0(\mathbf{r}_2). \quad (22)$$

Here $\exp(ik_0 \mathbf{n}_0 \cdot \mathbf{r}_1)$ is the plane wave, representing the motion of the incident electron in the direction of the unit vector \mathbf{n}_0 , when there is no interaction with the atom. Substituting (22) on the right-hand side of (16), we obtain

$$(\nabla^2 + k_n^2) F_n(\mathbf{r}_1) = \frac{8\pi^2 m}{\hbar^2} \int \left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_1} \right) \exp(ik_0 \mathbf{n}_0 \cdot \mathbf{r}_1) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) d\tau_2. \quad (23)$$

The solution of this equation with the correct asymptotic form (20) may be obtained by the method of Chap. VI, § 4, the solution being

$$F_n(\mathbf{r}) = \frac{2\pi m}{\hbar^2} \iint \frac{\exp(ik_n |\mathbf{r} - \mathbf{r}_1|)}{|\mathbf{r} - \mathbf{r}_1|} \exp(ik_0 \mathbf{n}_0 \cdot \mathbf{r}_1) \left(\frac{\epsilon^2}{r_1} - \frac{\epsilon^2}{r_{12}} \right) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) d\tau_1 d\tau_2. \quad (24)$$

The asymptotic form of this solution is§

$$F_n(\mathbf{r}) \sim \frac{2\pi m}{\hbar^2} r^{-1} e^{ik_n r} \iint \exp\{i(k_0 \mathbf{n}_0 - k_n \mathbf{n}) \cdot \mathbf{r}_1\} \left(\frac{\epsilon^2}{r_1} - \frac{\epsilon^2}{r_{12}} \right) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) d\tau_1 d\tau_2, \quad (25)$$

where \mathbf{n} is a unit vector in the direction of the vector \mathbf{r} . Hence

$$I_n(\theta) = \frac{k_n 4\pi^2 m^2}{k_0 \hbar^4} \left| \iint \exp\{i(k_0 \mathbf{n}_0 - k_n \mathbf{n}) \cdot \mathbf{r}_1\} \left(\frac{\epsilon^2}{r_1} - \frac{\epsilon^2}{r_{12}} \right) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) d\tau_1 d\tau_2 \right|^2. \quad (26)$$

It is possible to proceed further by this method of approximation, by substituting the expressions (24) for F_n in the function Ψ on the right-hand side of (16) and integrating the equations a second time, and so on. However, this method is very tedious|| in practice and it is better to start from more accurate initial approximations for Ψ in (16); these will be discussed later in §§ 5–8.

3. Two-body collisions in general

These results may be generalized to apply to the collision between any two atoms or molecules or ions. The motion of the system may be

† *Zeits. f. Physik*, 37 (1926), 863, and 38 (1926), 803.

‡ Cf. Chap. VII, § 1.

§ Cf. Chap. VII, § 1.

|| Cf. Chap. X, § 7.

described in terms of that of the centre of mass of the complete system, the relative motion of the centres of mass of the two bodies, and the motion of the individual particles of each body relative to the centre of mass of each. Of these the motion of the centre of mass of the complete system is irrelevant and may be separated out. The resulting equation may be compared with (12) above. The Hamiltonian equation (12) is compounded of three parts, namely,

$$(A) \left\{ \frac{\hbar^2}{8\pi^2m} \nabla_1^2 + \frac{1}{2}mv^2 \right\} F = 0,$$

representing the unperturbed motion of the incident particle;

$$(B) \left\{ \frac{\hbar^2}{8\pi^2m} \nabla_2^2 + \left(E_0 + \frac{\epsilon^2}{r_2} \right) \right\} \psi = 0,$$

representing the internal motion of the atomic electron; and

$$(C) \text{ minus the interaction energy, } \epsilon^2/r_1 - \epsilon^2/r_{12}.$$

Let us now see what terms must replace these in the general case. For the relative motion we have

$$\left\{ \frac{\hbar^2}{8\pi^2M} \nabla^2 + \frac{1}{2}Mv^2 \right\} F(\mathbf{r}) = 0, \quad (27)$$

where \mathbf{r} denotes the relative coordinates and M is the reduced mass of the system, i.e. if M_1, M_2 are the masses of the two bodies,

$$M = M_1 M_2 / (M_1 + M_2).$$

For the internal motion we have

$$\{H_a(\mathbf{r}_a) - E_a\}u(\mathbf{r}_a) = 0$$

and

$$\{H_b(\mathbf{r}_b) - E_b\}v(\mathbf{r}_b) = 0, \quad (28)$$

where H_a, H_b are the Hamiltonians of the unperturbed atoms. Corresponding to these equations there will be sets of proper values and proper functions

$$\begin{array}{cc} u_n(\mathbf{r}_a), & v_m(\mathbf{r}_b), \\ E_a^n, & E_b^m. \end{array}$$

For convenience of notation we shall not distinguish the two sets of functions, but shall denote each pair of states of the two systems by a single suffix n . The wave function $\psi_n(\mathbf{r}_a, \mathbf{r}_b)$ of the two systems will then be the product of two functions, $u_n(\mathbf{r}_a), v_m(\mathbf{r}_b)$, and the corresponding energy value E_n will be the sum $E_a^n + E_b^m$. ψ_n will satisfy the equation

$$\{H_a(\mathbf{r}_a) + H_b(\mathbf{r}_b) - E_a - E_b\}\psi = 0. \quad (29)$$

Finally, we have an interaction term $V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)$. The complete wave equation is now

$$\left[\frac{\hbar^2}{8\pi^2 M} \nabla_{\mathbf{r}}^2 - H_a(\mathbf{r}_a) - H_b(\mathbf{r}_b) + \frac{1}{2} M v^2 + E_0 - V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) \right] \Psi = 0, \quad (30)$$

and it is easily found by the method of § 2 that the differential cross-section (in relative coordinates) for the transition from state n to state m of the combined system will be given, within the range of validity of Born's first approximation, by

$$I_{n,m}(\theta) = \frac{4\pi^2 M^2 k_m}{\hbar^4 k_n} \left| \iint \int V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) \exp\{i(k_n \mathbf{n}_0 - k_m \mathbf{n}) \cdot \mathbf{r}\} \psi_m^* \psi_n d\tau_a d\tau_b d\tau \right|^2, \quad (31)$$

where

$$k_n = 2\pi M v / \hbar, \quad (32)$$

$$k_m^2 = \frac{8\pi^2 M}{\hbar^2} \left[\frac{1}{2} M v^2 + E_n - E_m \right],$$

and v is the initial relative velocity of the colliding systems. To obtain this differential cross-section in the coordinate system in which one of the bodies is initially at rest, it is only necessary to apply the classical laws of conservation of momentum and energy. The resulting formulae are given in § 10 of this chapter.

In the same way we may readily generalize all the formulae of § 2.

4. Rearrangement collisions

4.1. *Electron exchange*

As an example of the type of phenomenon to be considered under this heading, we return to the problem of § 2, namely, the collision between an electron and a hydrogen atom. We obtained in § 2 the probability that the incident electron should be scattered into a given solid angle after exciting the n th state. It is also possible that the incident electron may be captured into the n th state, and the atomic electron ejected. We refer to this phenomenon as electron exchange, and must now calculate its probability.

In order to calculate the probability of direct scattering, in § 2 we expanded the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ describing the collision in the form

$$\Psi = \left(\sum + \int \right) F_n(\mathbf{r}_1) \psi_n(\mathbf{r}_2), \quad (33)$$

where F_0 represents an incident wave and a scattered wave, and F_n a scattered wave, so long as the excitation energy of the state n is smaller than the energy of the incident electron. When this is no longer the

case, F_n falls off exponentially; the values of n in (33) which correspond to the continuous spectrum thus give us the possibility that the incident electron is captured and the atomic electron ejected. To obtain the probability of this event, we expand (33) in the alternative form

$$\Psi = \left(\sum_n + \int \right) G_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1). \quad (34)$$

Assuming† that G_n has asymptotic form

$$G_n \sim r^{-1}e^{ik_n r}g_n(\theta, \phi), \quad (35)$$

the probability that the incident electron is captured into the n th state, and the atomic electron ejected into the solid angle $d\omega$, is

$$\frac{k_n}{k_0} |g_n(\theta, \phi)|^2 d\omega. \quad (36)$$

We must state here that we may only treat the electrons as distinguishable in this way if the spins are antiparallel. For the scattering formulae with unpolarized beams, cf. § 4.3.

We must now show how to calculate g_n . The wave equation is

$$\left\{ \frac{\hbar^2}{8\pi^2m} (\nabla_1^2 + \nabla_2^2) + E + \frac{\epsilon^2}{r_1} + \frac{\epsilon^2}{r_2} - \frac{\epsilon^2}{r_{12}} \right\} \Psi = 0. \quad (37)$$

It was shown in § 2 that F_n satisfies

$$(\nabla^2 + k_n^2)F_n = \frac{8\pi^2m}{\hbar^2} \int \left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_1} \right) \Psi \psi_n^*(\mathbf{r}_2) d\tau_2. \quad (38)$$

In the same way, substituting (35) into (37), multiplying by $\psi_n^*(\mathbf{r}_1)$, and integrating over all x_1, y_1, z_1 , we obtain

$$(\nabla^2 + k_n^2)G_n(\mathbf{r}_2) = \frac{8\pi^2m}{\hbar^2} \int \left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_2} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2)\psi_n^*(\mathbf{r}_1) d\tau_1. \quad (39)$$

This equation is exact; to solve it, we assume various forms for Ψ on the right-hand side, and obtain a solution of the form (35) by the methods of § 2. It will be noticed that the *approximate* solution thus obtained is not an expansion of the approximate solution of § 2. In choosing an approximate Ψ we note that Ψ must satisfy

$$\begin{aligned} \int \{\Psi - F_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2)\}\psi_n^*(\mathbf{r}_2) d\tau_2 &= 0 \\ \int \{\Psi - G_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1)\}\psi_n^*(\mathbf{r}_1) d\tau_1 &= 0. \end{aligned} \quad (40)$$

If we require results valid only within the accuracy of Born's approximation, we take on the right-hand side of (39), as in § 2,

$$\Psi = \exp(ik_0 \mathbf{n}_0 \cdot \mathbf{r}_1)\psi_0(\mathbf{r}_2) \quad (41)$$

† No proof of this has at present been given, but a proof should be possible.

and obtain

$$[\nabla^2 + k_n^2]G_n = \frac{8\pi^2 m}{\hbar^2} \int \left\{ \frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_2} \right\} \psi_n^*(\mathbf{r}_1) \psi_0(\mathbf{r}_2) \exp(ik_0 \mathbf{n}_0 \cdot \mathbf{r}_1) d\tau_1. \quad (42)$$

Solving this equation by the method of Chap. VI, § 4, we obtain for the asymptotic form of G_n

$$G_n \sim r^{-1} \exp(ik_n r) g_n(\theta, \phi),$$

where

$$g_n(\theta, \phi) = -\frac{2\pi m}{\hbar^2} \iint \left\{ \frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_2} \right\} \psi_n^*(\mathbf{r}_1) \psi_0(\mathbf{r}_2) \exp i(k_0 \mathbf{n}_0 \cdot \mathbf{r}_1 - k_n \mathbf{n} \cdot \mathbf{r}_2) d\tau_1 d\tau_2 \quad (43)$$

and \mathbf{n} is a unit vector in the direction θ, ϕ . It is to be noted that the form (41) does not satisfy the equations (40), but for high-velocity impacts when Born's approximation is valid the error made is small. Further discussion of the equation (39) is given in Chap. X, § 6, and Chap. XI, § 5.

4.2. Rearrangement collisions in general

Before discussing the effect of the identity of the electrons on the formula for the scattered intensity we shall generalize the method to apply to rearrangement collisions in general. We require the probability that two systems A and B , in the n th and m th states respectively, become rearranged on impact, producing systems C and D in the s th and t th states respectively. In order to follow the method used for the simple case above, we must write the wave equation for the complete system in the form which is most relevant to the discussion of the final systems C and D . Instead of the coordinates which refer to the initial state, we choose now as coordinates the relative coordinates $\boldsymbol{\rho}$ of the centres of mass of the final systems, and the internal coordinates $\mathbf{r}_c, \mathbf{r}_d$ of the systems C and D referred to their respective centres of mass. The equation (30) may now be written

$$\left[-\frac{\hbar^2}{8\pi^2 M'} \nabla'^2 + H_c(\mathbf{r}_c) + H_d(\mathbf{r}_d) + V(\mathbf{r}_c, \mathbf{r}_d, \boldsymbol{\rho}) - E \right] \Psi = 0, \quad (44)$$

where M' is the reduced mass, $M_c M_d / (M_c + M_d)$, of the final systems, H_c, H_d the Hamiltonian operators of the internal motion of the bodies C and D , and $V(\mathbf{r}_c, \mathbf{r}_d, \boldsymbol{\rho})$ the interaction energy between C and D .

We distinguish a given pair of stationary states of the systems C and D by the suffix s and write the corresponding wave functions and energies as $\phi_s(\mathbf{r}_c, \mathbf{r}_d)$, E_s respectively. $\phi_s(\mathbf{r}_c, \mathbf{r}_d)$ is then the product of two wave functions $u_p(\mathbf{r}_c)$, $v_q(\mathbf{r}_d)$ of the separate systems, and E_s the

sum of the corresponding energy values, $E_c^p + E_d^q$. This notation corresponds exactly with that used in § 2.

Comparing the equation (44) with (37), we see that the formula of § 4.1 may be generalized by writing

$$\begin{aligned} M' \text{ for } m, & \quad \psi_0(\mathbf{r}_a, \mathbf{r}_b) \text{ for } \psi_0(\mathbf{r}_1), \\ -V(\mathbf{r}_c, \mathbf{r}_d, \boldsymbol{\rho}) \text{ for } \epsilon^2 \left(\frac{1}{r_2} - \frac{1}{r_{12}} \right), & \quad \phi_s(\mathbf{r}_c, \mathbf{r}_d) \text{ for } \psi_s(\mathbf{r}_2). \end{aligned}$$

To the accuracy of Born's first approximation, we obtain then, for the differential cross-section (in the relative coordinates $\boldsymbol{\rho}$) corresponding to the rearrangement in which the s th state of the systems C and D is excited, the formulae

$$\begin{aligned} I_s(\theta, \phi) d\omega &= (v_s/v) |g_s(\theta, \phi)|^2 d\omega \\ &= \frac{4\pi^2 M'^2 v_s}{h^4 v} \left| \int \int \int V(\mathbf{r}_c, \mathbf{r}_d, \boldsymbol{\rho}) \exp\{i(k\mathbf{n}_0 \cdot \mathbf{r} - k'_s \mathbf{n} \cdot \boldsymbol{\rho})\} \times \right. \\ &\quad \left. \times \psi_0(\mathbf{r}_a, \mathbf{r}_b) \phi_s(\mathbf{r}_c, \mathbf{r}_d) d\tau_a d\tau_b d\boldsymbol{\rho} \right|^2 d\omega, \quad (45) \end{aligned}$$

where $k = 2\pi Mv/h$, $k'_s = 2\pi M'v_s/h$, v , v_s being the initial and final relative velocities respectively.

As an example we may take the capture of electrons from atoms by α -particles. In this case \mathbf{r} is the vector distance between the centre of mass of the atom and the α -particle, $\boldsymbol{\rho}$ the distance between the centre of mass of the ionized atom and the centre of mass of the helium ion formed by the capture. For the internal coordinates we have initially the coordinates of the electron relative to the centre of mass of the atom and, finally, the coordinates of the same electron relative to the centre of mass of the helium ion. The application of the formula (45) for this case is discussed in Chap. XII, § 3.4.

4.3. *Effect of the exclusion principle on the scattering formulae†*

We return in this section to the problem of the scattering of electrons by a hydrogen atom. We limit ourselves to the case when the energy of the incident electron is so low that excitation is impossible. Then the collision is described by a wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ with asymptotic form

$$\begin{aligned} \Psi &\sim [\exp ikz_1 + r_1^{-1} f(\theta_1) \exp ikr_1] \psi(r_2) \quad (r_1 \text{ large}), \\ &\sim [r_2^{-1} g(\theta_2) \exp ikr_2] \psi(r_1) \quad (r_2 \text{ large}). \end{aligned}$$

If the electrons were distinguishable one could deduce that the number

† Oppenheimer, *Phys. Rev.* **32** (1928), 361.

of electrons scattered was proportional to $|f|^2$, and the number ejected to $|g|^2$. However, as shown in Chapter V, one must use antisymmetrical wave functions. The wave function symmetrical or antisymmetrical in the space coordinates is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \pm \Psi(\mathbf{r}_2, \mathbf{r}_1),$$

which has asymptotic form, for large r_1 , say,

$$[e^{ikz_1} + \{f(\theta) \pm g(\theta)\} r_1^{-1} e^{ikr_1}] \psi(r_2).$$

Using either formula, one obtains the result that the number of electrons scattered or knocked into the solid angle $d\omega$ is

$$|f(\theta) \pm g(\theta)|^2 d\omega.$$

As shown in Chap. V, § 5, we must combine these formulae in the ratio 1 to 3 for unpolarized electrons. The total number scattered into the solid angle $d\omega$ is thus

$$\left\{ \frac{3}{4} |f-g|^2 + \frac{1}{4} |f+g|^2 \right\} d\omega. \quad (46)$$

Let us now consider the case of electron collisions with helium. We denote the second atomic electron by the suffix 3, so the collision is described by a wave function

$$\begin{aligned} \Psi &\sim \{e^{ikz_1} + f(\theta_1) r_1^{-1} e^{ikr_1}\} \psi(r_2, r_3) && (r_1 \text{ large}), \\ &\sim g(\theta_2) r_2^{-1} e^{ikr_2} \psi(r_1, r_3) && (r_2 \text{ large}), \\ &\sim g(\theta_3) r_3^{-1} e^{ikr_3} \psi(r_2, r_1) && (r_3 \text{ large}). \end{aligned}$$

By following through an argument very similar to that used above for hydrogen, we find that the total number of electrons scattered into the solid angle $d\omega$ is

$$|f-g|^2 d\omega. \quad (47)$$

5. Approximate methods for slow collisions. The method of distorted waves

The first approximation in Born's method is only valid when the energy of relative motion in the collision is great compared with the energy of the internal motions involved. For an important class of collisions this condition is not satisfied, and it is necessary to develop methods of practical value for such cases. We shall describe four methods, to be referred to respectively as the methods of distorted waves, of the strongly coupled equations, of perturbed stationary states, and of the collision complex. In this section we discuss the first of these.

Generalizing formula (16) of § 2, we see that the functions $F_n(\mathbf{r})$ satisfy the series of equations

$$[\nabla^2 + k_n^2]F_n(\mathbf{r}) = \frac{8\pi^2 M}{\hbar^2} \int \int V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) \Psi \psi_n^* d\tau_a d\tau_b \quad (n = 0, 1, 2, \dots). \quad (48)$$

Writing
$$\Psi = \sum_m F_m(\mathbf{r}) \psi_m(\mathbf{r}_a, \mathbf{r}_b),$$

and
$$V_{nm}(\mathbf{r}) = \int V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) \psi_n \psi_m^* d\tau_a d\tau_b, \quad (49)$$

we have
$$(\nabla^2 + k_n^2)F_n(\mathbf{r}) = \frac{8\pi^2 M}{\hbar^2} \sum_m F_m V_{mn}. \quad (50)$$

Born's approximation is obtained by taking on the right-hand side of (50)
$$F_0 = \exp(ik_0 \mathbf{n}_0 \cdot \mathbf{r}); \quad F_m = 0 \quad (m \neq 0).$$

We make now the less drastic assumption that the non-diagonal matrix elements V_{nm} are so small that we may neglect all products on the right-hand side except $V_{nn}F_n$ and $V_{0n}F_0$, which involves the incident wave. We obtain thus the series of equations

$$\left[\nabla^2 + k_0^2 - \frac{8\pi^2 M}{\hbar^2} V_{00} \right] F_0(\mathbf{r}) = 0, \quad (51.1)$$

$$\left[\nabla^2 + k_n^2 - \frac{8\pi^2 M}{\hbar^2} V_{nn} \right] F_n(\mathbf{r}) = \frac{8\pi^2 M}{\hbar^2} V_{0n}(\mathbf{r}) F_0(\mathbf{r}) \quad (n \neq 0). \quad (51.2)$$

If $V_{00}(\mathbf{r})$, $V_{nn}(\mathbf{r})$ are spherically symmetrical, one may obtain a formal solution of these equations, satisfying the boundary conditions (19), (20), by the methods of Chapters II and VI. In Chap. II, eq. (16), a solution of equation (51.1) was obtained satisfying the boundary condition (19), i.e. having the asymptotic form

$$e^{ik_0 z} + f(\theta) r^{-1} e^{ik_0 r}. \quad (52)$$

We denote this solution by $F_0(\mathbf{r})$.

If we substitute this form for $F_0(\mathbf{r})$ in the right-hand side of (51.2), we obtain an inhomogeneous equation for $F_n(\mathbf{r})$ of the form

$$\left[\nabla^2 + k_n^2 - \frac{8\pi^2 M}{\hbar^2} V_{nn}(r) \right] F_n = s_n(r, \theta, \phi). \quad (53)$$

The problem of obtaining solutions of this equation with the asymptotic form (20) has been solved in Chap. VI, § 3. If we denote by $\mathfrak{F}_n(r, \theta)$ the solution of the homogeneous equation

$$\left[\nabla^2 + k_n^2 - \frac{8\pi^2 M}{\hbar^2} V_{nn}(r) \right] \mathfrak{F} = 0 \quad (54)$$

which has the asymptotic form

$$\mathfrak{F}_n(r, \theta) \sim e^{ik_n z} + r^{-1} e^{ik_n r} \times \text{function of } \theta,$$

the asymptotic form of the required solution of (51.2) is

$$F_n(\mathbf{r}) \sim -r^{-1} e^{ik_n r} \frac{2\pi M}{h^2} \int V_{0n}(\mathbf{r}') F_0(r', \theta') \mathfrak{F}_n(r', \pi - \Theta) d\tau', \quad (55)$$

$$\text{where} \quad \cos \Theta = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi'), \quad (56)$$

θ being the angle of scattering. Referring to (20) and (21), we see that the differential cross-section corresponding to excitation of the n th state is now given in relative coordinates by

$$I_n(\theta) = \frac{k_n}{k_0} \frac{4\pi^2 M^2}{h^4} \left| \iiint V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) \psi_0 \psi_n^* F_0(r', \theta') \mathfrak{F}_n(r', \pi - \Theta) d\tau_a d\tau_b d\tau \right|^2. \quad (57)$$

This formula reduces to Born's expression (31) if we take the functions F_0 , \mathfrak{F}_n to be plane waves. We see then that this method takes into account the distortion of the incident and outgoing waves by the scattering field. The function $F_0(r, \theta)$ represents the motion of the electron in the field $V_{00}(r)$ of the initial state, $\mathfrak{F}_n(r', \pi - \Theta)$ that in the field $V_{nn}(r)$ of the excited state.

Formula (57) is applied in Chap. XI, § 5, to the scattering of electrons by atoms, and in Chap. XII, § 3.5, to the excitation of vibration and rotation in molecular collisions.

A similar formula may be derived for rearrangement collisions. Thus in formula (45) the plane waves $e^{ik_n \cdot \mathbf{r}}$, $e^{-ik_i \cdot \mathbf{r}}$ are replaced by $F_0(r, \theta)$, $\mathcal{G}_s(\rho, \pi - \vartheta)$, where F_0 , \mathcal{G}_s are the proper solutions of

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2} V_{00} \right] F_0 = 0,$$

$$\left[\nabla'^2 + k_s'^2 - \frac{8\pi^2 M'}{h^2} U_{ss} \right] \mathcal{G}_s = 0,$$

which have the asymptotic forms of a plane wave and the corresponding scattered wave. V_{00} and U_{ss} are given by

$$V_{00} = \iint V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) |\psi_0|^2 d\tau_a d\tau_b,$$

$$U_{ss} = \iint V(\mathbf{r}_c, \mathbf{r}_d, \rho) |\phi_s|^2 d\tau_c d\tau_d.$$

6. Approximate methods for slow collisions. The case of strong coupling

6.1. The case of exact resonance

The validity of the previous method of approximation depends on the smallness of the non-diagonal matrix-elements of the interaction energy.

In considering the excitation of the n th stationary state by the impact it is thus only necessary to include the interaction of two waves, the incident and elastically scattered, and that scattered after excitation of the n th state. Further, the effect of the reaction of the inelastic on the elastic scattering need not be taken into account. We may therefore regard the method as one of successive approximations to the solution of the simultaneous equations†

$$\begin{aligned} [\nabla^2 + k_0^2 - (8\pi^2 M/h^2)V_{00}]F_0 &= (8\pi^2 M/h^2)V_{0n}F_n, \\ [\nabla^2 + k_n^2 - (8\pi^2 M/h^2)V_{nn}]F_n &= (8\pi^2 M/h^2)V_{0n}F_0, \end{aligned} \quad (58)$$

on the assumption that the matrix-element V_{0n} is small. Now in certain other cases it is sufficient to consider the interaction of two states only, but the matrix-element $V_{0n}(\mathbf{r})$ associated with these states may not be small. Such cases occur when the states 0, n are nearly in resonance, i.e. the energy difference ΔE between the states is small compared with that between any other pair of states. We then obtain as before the simultaneous equations (58), but the method of successive approximations is not in general applicable. It is then more difficult to obtain a satisfactory method of treatment.

In the special case of exact resonance between the two states (as, for example, in considering electron transfer from a helium atom to a helium positive ion) we may obtain an exact solution, but for other cases more complicated methods must be used. We first consider the special case.

Writing $k_0^2 = k_n^2 = k^2$ in (58), and assuming that the field V_{nn} is the same as V_{00} , we obtain the equations

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2} V_{00}(r) \right] F_0(\mathbf{r}) = \frac{8\pi^2 M}{h^2} V_{0n}(\mathbf{r}) F_n(\mathbf{r}), \quad (59.1)$$

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2} V_{00}(r) \right] F_n(\mathbf{r}) = \frac{8\pi^2 M}{h^2} V_{0n}(\mathbf{r}) F_0(\mathbf{r}). \quad (59.2)$$

These equations must be solved subject to the boundary conditions that for large r

$$\begin{aligned} F_0(\mathbf{r}) &\sim e^{ikz} + r^{-1} e^{ikr} f_0(\theta, \phi), \\ F_n(\mathbf{r}) &\sim r^{-1} e^{ikr} f_n(\theta, \phi). \end{aligned} \quad (60)$$

By addition and subtraction of (59.1), (59.2) we obtain the independent equations

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2} \{V_{00} + V_{0n}\} \right] \{F_0 + F_n\} = 0, \quad (61.1)$$

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2} \{V_{00} - V_{0n}\} \right] \{F_0 - F_n\} = 0. \quad (61.2)$$

† It is assumed that $V_{0n} = V_{n0}$.

If the functions V_{00} , V_{0n} are spherically symmetrical, we may solve these equations by the method of Chapter II. We obtain (Chap. II, eq. (17)) solutions of asymptotic form

$$F_0 + F_n \sim \frac{1}{2} \left[e^{ikz} + e^{ikr} \frac{1}{2ikr} \sum_s (2s+1)(e^{2i\eta_s} - 1) P_s(\cos \theta) \right], \quad (62.1)$$

$$F_0 - F_n \sim \frac{1}{2} \left[e^{ikz} + e^{ikr} \frac{1}{2ikr} \sum_s (2s+1)(e^{2i\delta_s} - 1) P_s(\cos \theta) \right]. \quad (62.2)$$

For definitions of the phases, η_s , δ_s , cf. Chap. II, § 1. Solving (62) for F_n , we obtain

$$F_n \sim r^{-1} e^{ikr} \frac{1}{4ik} \sum_s (2s+1)(e^{2i\eta_s} - e^{2i\delta_s}) P_s(\cos \theta). \quad (63)$$

The differential cross-section corresponding to transfer of excitation will then be

$$I_n(\theta) d\omega = \frac{1}{16k^2} \left| \sum_s (e^{2i\eta_s} - e^{2i\delta_s})(2s+1) P_s(\cos \theta) \right|^2 d\omega, \quad (64)$$

and the total cross-section

$$Q_n = \frac{\pi}{k^2} \sum_s (2s+1) \sin^2(\eta_s - \delta_s). \quad (65)$$

The maximum partial cross-section for charge transfer between particles of given relative angular momentum (given s) is $(2s+1)\pi/k^2$ in agreement with § 1(9).

We are now in a position to examine the condition of validity of the method of distorted waves described above in § 3.1. Applying this method to the problem discussed in this section, we obtain, since $V_{00} = V_{nn}$, the formula

$$Q_n = \frac{8\pi^3 M^2}{h^4} \int_0^\pi \left| \int V_{0n}(r') F_0(r', \theta') \mathfrak{F}_0(r', \pi - \Theta) dr' \right|^2 \sin \theta d\theta. \quad (66)$$

Using the expansions

$$F_0(r, \theta) = \frac{1}{k} \sum_s (2s+1) i^s e^{i\gamma_s} F_0^s(r) P_s(\cos \theta),$$

$$\mathfrak{F}_0(r, \pi - \Theta) = \frac{1}{k} \sum_s (2s+1) i^{-s} e^{i\gamma_s} F_0^s(r) P_s(\cos \Theta), \quad (67)$$

we obtain

$$Q_n = \frac{\pi}{k^2} \sum_s (2s+1) \left\{ \frac{16\pi^2 M}{kh^2} \int V_{0n} \{ F_0^s(r) \}^2 r^2 dr \right\}^2. \quad (68)$$

To prove the validity of the method of distorted waves we must demonstrate the approximate equality of the expressions

$$\sin(\eta_s - \delta_s), \quad \frac{16\pi^2 M}{k\hbar^2} \int V_{0n} \{F_0^s(r)\}^2 r^2 dr. \quad (69)$$

Provided both quantities are small, this may be shown by the method of Chap. II, § 2. Thus the condition of validity of the method of distorted waves is that the second expression in (69) should be small compared with unity. The range of validity of the distorted wave method

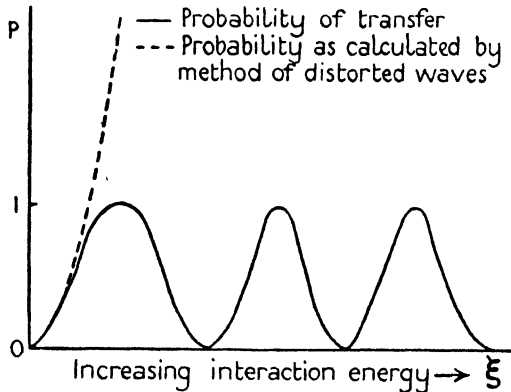


FIG. 18.

of approximation for the calculation of the probability of transfer of excitation is illustrated in general terms in Fig. 18, which also shows the manner in which the approximate method becomes inaccurate.

In this figure the probability P of energy transfer for a given relative angular momentum is represented as a function of a parameter ξ which is taken to indicate the effective magnitude of V_{0n} . The relative velocity of the impacts is considered fixed. As ξ increases, the probability of transfer will increase from zero towards a value unity. After this value is attained the probability will oscillate as shown. The distorted wave method of approximation is valid only in the region of the initial increase of probability from zero. It predicts a monotonic increase of probability with ξ , and we must expect it always to indicate too great a probability of the transfer process. Similar behaviour will be manifest in the behaviour of the probability as a function of relative velocity of impact, for a fixed value of the parameter ξ . Thus at low velocities the distorted wave method will give too large a probability.†

† Cf. Chap. XI, §§ 3.2, 3.3, 5.2; Chap. XII, § 3.

6.2. Inexact resonance

When the resonance is no longer exact, no exact analytical solution of the coupled equations (58) can be obtained. However, in most cases of practical importance the wave numbers k and k_n are very large when measured in atomic units, $1/a_0$. The variation of V_{00} , V_{nn} , and V_{0n} is then very small within a wave-length and an extension of Jeffreys's method (Chap. I, § 6, and Chap. VII, § 6.2) may be used to obtain an approximate solution, valid particularly when the potentials are large.

The problem is to obtain solutions F_0^l , F_n^l of the equations

$$\left[\frac{d^2}{dr^2} + k^2 - U_{00} - \frac{l(l+1)}{r^2} \right] F_0^l = U_{0n} F_n^l, \quad (70)$$

$$\left[\frac{d^2}{dr^2} + k_n^2 - U_{nn} - \frac{l(l+1)}{r^2} \right] F_n^l = U_{0n} F_0^l, \quad (71)$$

which are proper functions with asymptotic form

$$F_0^l \sim \frac{i^l}{k} (2l+1) \exp(i\eta_0^l) \left[\sin(kr - \frac{1}{2}l\pi + \eta_0^l) + q_0^l \exp\{i(kr - \frac{1}{2}l\pi + \eta_0^l)\} \right], \quad (72)$$

$$F_n^l \sim \frac{i^l}{k_n} (2l+1) q_n^l \exp(ik_n r). \quad (73)$$

The effective cross-sections Q_0 , Q_n , for elastic and inelastic collisions respectively, are then given by

$$Q_0 = \frac{4\pi}{k^2} \sum (2l+1) \{ |q_0^l|^2 + \sin^2 \eta_0^l - |q_0^l| \sin \eta_0^l \cos \eta_0^l \}, \quad (74)$$

$$Q_n = \frac{4\pi}{kk_n} \sum (2l+1) |q_n^l|^2. \quad (75)$$

Stueckelberg† obtained a 'classical' approximation, essentially an extension of Jeffreys's method to the coupled equations, by expanding F_0^l in the form

$$F_0^l = r^{-1} \exp\{h^{-1}(S_0 + hS_1 + h^2S_2 + \dots)\}. \quad (76)$$

The equation obtained for F_0^l by elimination of F_n^l from (65) may be then solved by neglecting terms of degree greater than unity in h .

The form of the solution depends on whether the function $f_0(r) - f_n(r)$ has a real positive zero R or not, f_0 and f_n being given by

$$f_0 = k^2 - U_{00} - \frac{l(l+1)}{r^2}, \quad (77)$$

$$f_n = k_n^2 - U_{nn} - \frac{l(l+1)}{r^2}. \quad (78)$$

† *Helv. Phys. Acta*, 5 (1932), 370.

The case of most interest is the one in which R does exist. Stueckelberg finds then that

$$|q_n^l|^2 = \frac{k_n}{k} e^{-2\delta} (1 - e^{-2\delta}) \sin^2 \tau, \quad (79)$$

where $\delta = [(2\pi)^\dagger U_{0n}^2 / \{2(U'_{00} - U'_{nn})(f_0 + \sqrt{(f_0^2 - U_{0n}^2)})^\ddagger\}]_{r=R}$, (80)

and $\tau = \int g_0^\ddagger dr - \int g_n^\ddagger dr$, (81)

the lower limits in each case being the zero of the integrand and

$$g_0, g_n = \frac{1}{2}(f_0 + f_n) \pm \frac{1}{2}\{(f_0 - f_n)^2 + 4U_{0n}^2\}^\ddagger. \quad (82)$$

We now consider the relation of this formula to that given by the method of distorted waves

$$|q_n^l|^2 = \frac{1}{k^2} \left| \int_0^\infty U_{0n} \mathfrak{F}_0^l(r) \mathfrak{F}_n^l(r) dr \right|^2, \quad (83)$$

where \mathfrak{F}_0^l , \mathfrak{F}_n^l are the appropriate solutions of (70) and (71) with the right-hand sides equal to zero.† By substituting the approximations‡

$$\mathfrak{F}_0^l(r) \simeq (k^2/f_0)^\ddagger \sin\{\frac{1}{4}\pi + f_0^\ddagger\} \quad (r > r_0), \quad (84)$$

$$\mathfrak{F}_n^l(r) \simeq (k_n^2/f_n)^\ddagger \sin\{\frac{1}{4}\pi + f_n^\ddagger\} \quad (r > r_n), \quad (85)$$

r_0 , r_n being the respective zeros of f_0 and f_n , and ignoring contributions arising from $r < r_0, r_n$ in which the functions are decreasing exponentially as r decreases, we find, by the application of the method of steepest descents§

$$|q_n^l|^2 = 2 \frac{k_n}{k} \delta_0 \sin^2 \tau_0, \quad (86)$$

where δ_0 differs from δ only in that $(f_0^2 - U_{0n}^2)^\ddagger$ is replaced by f_0^\ddagger and τ_0 from τ in the replacement of g_0 and g_n by f_0 and f_n respectively. Thus, comparing (86) with (80) we see that, under 'classical conditions', in which k and k_n are large, the method of distorted waves will give a good approximation if

$$\pi^\ddagger U_{0n}^2 / \{2(U'_{00} - U'_{nn})f_0^\ddagger\}_{r=R} \ll 1. \quad (87)$$

In view of the classical conditions which prevail when the formula (80) is valid it is to be expected that a detailed picture of the process can be given. Fig. 19(a) represents the initial and final potential energy curves for the reaction. At infinite separation the two curves must tend

† $\mathfrak{F}_0, \mathfrak{F}_n$ must vanish at $r = 0$ and have the asymptotic forms

$$\mathfrak{F}_0 \sim \sin(kr - \frac{1}{2}\pi + \zeta_0), \quad \mathfrak{F}_n \sim \sin(k_n r - \frac{1}{2}\pi + \kappa_n).$$

‡ See Chap. I, § 6, and Chap. VII, § 6.2.

§ H. and B. Jeffreys, *Methods of Mathematical Physics*, Cambridge (1947), p. 472.

to limits differing in energy by $\hbar^2(k^2 - k_n^2)/2M$. In the absence of interaction between the two levels the curves would cross at $r = R$ and there would be no probability of a transition. A finite value of U_{0n} prevents crossing and the shape of the curves in the neighbourhood of $r = R$ is as shown in Fig. 19(b).

We may now follow the course of events as the systems approach from the initial state *A*. On arriving at the crossing-point there is a chance *P* that the systems will jump from curve I to curve II. In either case they will continue to approach until the repulsive barrier

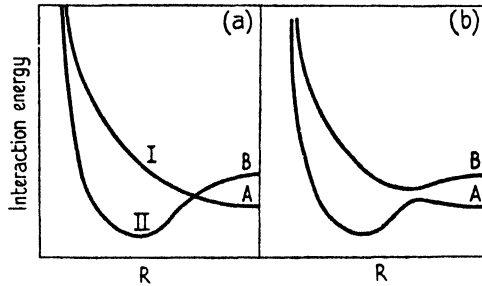


FIG. 19. Illustrating the interaction of potential curves at a crossing-point.

becomes too large, after which they will again begin to separate. On return to the crossing-point there will be a chance *P* of a jump from either curve to the other. The total chance that, after finally separating from the crossing-point, the systems will be found on curve II instead of curve I will be $2P(1-P)$. Landau† and Zener‡ have independently calculated *P* under classical conditions and they obtain, in terms of (80), $P = e^{-2\delta}$. This is what we would expect from Stueckelberg's result for, in view of (79), the average partial cross-section should be

$$4\pi P(1-P)(2l+1)/k^2.$$

The second point to notice is that the partial cross-section $|q_n^l|^2$ is small, not only when δ is small, but also when it is large. In the latter case, which arises either when, at the crossing-point, U_{0n} is large, the velocity Mf_0/\hbar is small, or the difference in slope of the potential curves is small, we have adiabatic conditions.

To obtain the total cross-section use may be made of the fact that q_n^l becomes very small for such values of *l* that the zeros of the functions

† *Z. Phys. Sow. Un.* 2 (1932), 46.

‡ *Proc. Roy. Soc. A*, 137 (1932), 696.

f_0, f_n lie outside the crossing-point. This will occur approximately when $l = kR$ or $k_n R$, whichever is the smaller. Hence

$$Q_n \simeq \frac{8\pi}{k^2} \int_0^{kR, k_n R} e^{-2\delta}(1-e^{-2\delta})l \, dl$$

$$\triangleright \pi R^2. \quad (88)$$

To obtain a large cross-section it is necessary, not only that R should be large, but also that δ should not be too large or too small for most values of l . This matter will be discussed in further detail in Chap. XII, § 3.3, in connexion with transfer of excitation and of charge between slowly moving atoms and ions.

The case where no crossing-point exists is at least as important for the discussion of slow collisions between atoms. It has also been considered with the classical approximation by Stueckelberg.† However, as the formulae obtained are not of such wide generality as for the case discussed above we defer consideration of them until Chap. XII, § 3.3, where they will be applied to specific problems.

6.3. *Rearrangement collisions*

The theory of the preceding section may be applied to rearrangement collisions involving electron transfer between two atoms or ions, provided the change of momentum of the electron transfer may be neglected. This change is zero in the case of exact resonance and may also be ignored for collisions in which the atoms are moving slowly compared with the atomic electrons. For fast collisions it cannot be ignored, but Born's approximation (45) may then be applied (see Chap. XII, § 2.2).

In other rearrangement collisions the strong coupling method is much more difficult to apply, for the appropriate simultaneous equations for the functions F_0 and G_s are no longer differential but integro-differential. The problem of electron exchange in elastic scattering will be discussed in terms of these equations in Chap. X, § 5. Otherwise no attempt has yet been made to use them.

7. **Approximate methods for slow collisions. The method of perturbed stationary state wave functions**

In calculating the probability of excitation of a given state by the previous methods we have neglected altogether the interaction of all the states except the initial state and the state under consideration.

† Loc. cit.

This neglect may often be serious. We now consider a method which is applicable under nearly adiabatic conditions, the relative velocity of the colliding systems being slow throughout the encounter. It depends on the use of stationary state wave functions which are already perturbed by the interaction of the colliding particles, treated as though at relative rest. The kinetic energy of the relative motion is then introduced as the small perturbation producing the transitions. This procedure does include a partial allowance for interaction between different states as the perturbation of the stationary state wave functions need not be small.

We restrict ourselves to cases where both systems are spherically symmetrical.

As before, we have to solve the equation

$$\left[\frac{\hbar^2}{8\pi^2 M} \nabla_r^2 - H_a(\mathbf{r}_a) - H_b(\mathbf{r}_b) - V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) + E \right] \Psi = 0, \quad (89)$$

with the usual boundary conditions. We first consider the equation

$$[H_a(\mathbf{r}_a) + H_b(\mathbf{r}_b) + V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) - E(r)]\chi = 0 \quad (90)$$

in which \mathbf{r} , the relative coordinates of the two systems, appear as parameters. We assume that a solution may be obtained for any value of \mathbf{r} , leading to a set of proper functions $\chi_n(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)$ and proper values $\epsilon_n(r)$. These functions are classified by their behaviour for large r . We distinguish by the suffix n that energy value which tends, as $r \rightarrow \infty$, to E_n , the n th value of the equation

$$[H_a(\mathbf{r}_a) + H_b(\mathbf{r}_b) - E]\Psi = 0. \quad (91)$$

The energy $\epsilon_n(r)$ may then be written

$$\epsilon_n(r) = E_n - \eta_n(r), \quad (92)$$

where $\eta_n \rightarrow 0$ as $r \rightarrow \infty$. The functions χ_n form an orthogonal normal set with respect to the coordinates $\mathbf{r}_a, \mathbf{r}_b$ for all values of the parameter \mathbf{r} . It is therefore possible to expand Ψ in the form

$$\Psi = \sum_n \chi_n(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) F_n(\mathbf{r}), \quad (93)$$

and, as before, we require solutions for the functions $F_n(\mathbf{r})$ which have the asymptotic form (20), representing outgoing waves.

On substitution in (89), remembering that

$$[-H_a(\mathbf{r}_a) - H_b(\mathbf{r}_b) - V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)]\chi_n = [\eta_n(r) - E_n]\chi_n, \quad (94)$$

we obtain

$$\begin{aligned} \sum_n \frac{\hbar^2}{8\pi^2 M} [F_n \nabla_r^2 \chi_n + 2 \text{grad}_r F_n \cdot \text{grad}_r \chi_n + \chi_n \nabla_r^2 F_n] \\ = \sum_n [E_n - \eta_n(r) - E] \chi_n F_n. \end{aligned} \quad (95)$$

We now multiply both sides of this equation by χ_n^* and integrate over the coordinate space of \mathbf{r}_a and \mathbf{r}_b . Using the relation

$$\iint \chi_n^* \text{grad}_r \chi_n d\tau_a d\tau_b = 0,$$

we obtain

$$\begin{aligned} \frac{\hbar^2}{8\pi^2 M} \nabla^2 F_n + [E - E_n + \eta_n(r)] F_n = - \sum_m F_m(r) \frac{\hbar^2}{8\pi^2 M} \iint \chi_n^* \nabla_r^2 \chi_m d\tau_a d\tau_b - \\ - 2 \sum_{m \neq n} \frac{\hbar^2}{8\pi^2 M} \text{grad} F_m(\mathbf{r}) \cdot \iint \chi_n^* \text{grad}_r \chi_m d\tau_a d\tau_b. \end{aligned}$$

These equations replace equations (48), which were obtained by expanding in a series of unperturbed stationary state wave functions. To obtain approximate solutions we use methods exactly similar to those used in § 5.

Neglecting non-diagonal matrix-elements, except those referring to the initial state, we obtain

$$\begin{aligned} \nabla^2 F_0 + \left[\frac{8\pi^2 M}{\hbar^2} \{E - E_0 + \eta_0(r)\} + \iint \chi_0^* \nabla_r^2 \chi_0 d\tau_a d\tau_b \right] F_0 = 0, \\ \nabla^2 F_n + \left[\frac{8\pi^2 M}{\hbar^2} \{E - E_n + \eta_n(r)\} + \iint \chi_n^* \nabla_r^2 \chi_n d\tau_a d\tau_b \right] F_n \\ = -F_0 \iint \chi_n^* \nabla_r^2 \chi_0 d\tau_a d\tau_b - 2 \text{grad} F_0 \cdot \iint \chi_n^* \text{grad}_r \chi_0 d\tau_a d\tau_b. \end{aligned} \quad (96)$$

These inhomogeneous equations may be solved in the same way as the equations (51.1), (51.2).

In order to compare these equations with those obtained by the method of expansion in unperturbed stationary state wave functions, we will use as the functions χ_n those obtained from (94) by a first-order perturbation calculation, treating V as small. To this approximation we obtain by the usual method†

$$\begin{aligned} \chi_n &= \psi_n + \sum_{m \neq n} V_{mn} \psi_m / (E_n - E_m) \\ &= -\eta_n + V_{nn} + \sum_{m \neq n} \frac{V_{nm} V_{mn}}{E_n - E_m}, \end{aligned}$$

† Cf. Sommerfeld, *Wave Mechanics*, p. 144.

where
$$V_{nm} = \iint V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) \psi_m^*(\mathbf{r}_a, \mathbf{r}_b) \psi_n(\mathbf{r}_a, \mathbf{r}_b) d\tau_a d\tau_b.$$

We thus obtain from (96)

$$\begin{aligned} & \nabla^2 F_n + \\ & + \left[\frac{8\pi^2 M}{\hbar^2} \{E - E_n - V_{nn}(r)\} + \sum_{m \neq n} \frac{V_{mn}}{(E_m - E_n)^2} \left\{ \nabla_r^2 + \frac{8\pi^2 M}{\hbar^2} (E_m - E_n) \right\} V_{nm} \right] F_n \\ & = -F_0 \left[\frac{\nabla^2 V_{0n}}{E_0 - E_n} - \sum_{m \neq n, 0} \frac{V_{mn} \nabla_r^2 V_{0m}}{(E_n - E_m)(E_m - E_0)} - \right. \\ & \quad \left. - 2 \operatorname{grad}_r F_0 \cdot \left[\frac{\operatorname{grad}_r V_{0n}}{E_0 - E_n} - \sum_{m \neq n} \frac{V_{mn} \operatorname{grad}_r V_{0m}}{(E_n - E_m)(E_m - E_0)} \right] \right]. \quad (97) \end{aligned}$$

If we neglect on the right-hand side of (97) matrix elements involving states other than 0 and n , we obtain the equation

$$\begin{aligned} & \nabla^2 F_n + \frac{8\pi^2 M}{\hbar^2} \{E - E_n - V_{nn}(r)\} F_n \\ & = -F_0 \nabla^2 V_{0n} / (E_n - E_0) - 2 \operatorname{grad} F_0 \cdot \operatorname{grad} V_{0n} / (E_n - E_0). \end{aligned}$$

Solving this equation by the same method as that used in § 3.1 and using the differential equation for F_0 , we obtain, for the differential cross-section corresponding to the excitation, the formula

$$\begin{aligned} & I_n(\theta) d\omega \\ & = \frac{k_n}{k_0} \frac{4\pi^2 M^2}{\hbar^4} \left| \int \left(1 - \frac{8\pi^2 M}{\hbar^2} \frac{V_{00} - V_{nn}}{k^2 - k_n^2} \right) V_{0n}(\mathbf{r}') F_0(r', \theta') \mathfrak{F}_n(r', \pi - \Theta') d\tau' \right|^2. \end{aligned}$$

We see that, apart from the term $(V_{00} - V_{nn}) / (k^2 - k_n^2)$, this formula reduces to that obtained from the method of distorted waves. Exact equivalence of the two formulae would not be expected owing to the different initial assumptions. Provided $V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)$ is small, the formula reduces to Born's approximation for high velocities of impact, but this is not so when the interaction is large. Under the latter conditions the method described in this section is only valid when the relative velocity of the impact is small compared with that of the internal motions concerned.

However, if it is possible to obtain the perturbed stationary state wave functions with a reasonable degree of accuracy, the calculation of the scattered amplitudes by the method of this section should lead to results of greater accuracy than the previous methods, the interaction of the higher states being automatically included to some extent in the initial approximations. It is best suited to the discussion of ionization and excitation of atoms by heavy particles such as positive ions or

mesons when the velocity of relative motion is less than the orbital velocity of the atomic electrons concerned. Owing, however, to the comparative difficulty of obtaining accurate perturbed functions, the method has not yet been applied extensively. The applications which have been made are discussed in Chap. XII, § 3.4.

8. The method of the collision complex

The general scattering problem involves the solution of the infinite set of simultaneous equations (50)

$$(\nabla^2 + k_n^2)F_n(r) = \frac{8\pi^2 M}{\hbar^2} \left(\sum + \int \right) V_{nm} F_m \quad (n = 0, 1, 2, \dots), \quad (98)$$

subject to the boundary conditions

$$F_0(r) \sim e^{ikz} + r^{-1}f(\theta, \phi)e^{ikr}, \quad F_n(r) \sim r^{-1}f_n(\theta, \phi)e^{ik_n r}. \quad (99)$$

Various approximations have been discussed which depend on the smallness of all but a very limited number of terms on the right-hand side. We now consider what can be done when many of the interactions V_{nm} are large.

For the sake of argument we consider the impact of a single particle with some system comprising several particles. This system will be referred to occasionally as the struck nucleus since the method is especially important for nuclear phenomena (see Chap. XIII). If many of the quantities V_{nm} are large for $r < R$, it follows that, when the incident particle approaches to within a distance R , the energy becomes rapidly distributed among a great number of other modes of motion. This interchange will continue until sufficient energy concentrates in one mode which corresponds to escape of one or more particles from the system. In other words, when the incident particle penetrates within a distance R there is a high probability of it forming with the particles of the struck system an excited complex of considerable lifetime.

Corresponding to the fact that no emission of particles can take place until sufficient energy concentrates in the appropriate mode of motion, the complex can be regarded as similar to a stable molecule or atomic nucleus except for motion in a limited number of modes—it can be described by a linear combination of wave functions most of the important members of which are of closed form. Thus the equations (98) are derived by expanding the wave function Ψ , describing the collision, in the form

$$\Psi = \left(\sum + \int \right) F_n(r) \psi_n(r_a). \quad (100)$$

This expansion includes, in general, terms in which both ψ_n and F_n are bound functions, k_n^2 in (98) being negative. When the V_{nm} are large, such terms in the expansion (100) will play a very important part and correspond as a whole to the collision complex.

The collision complex will possess a system of energy-levels which will not be quite sharp owing to the finite though slow rate at which it breaks up. If the width of the levels is smaller than their spacing, resonance effects are to be expected when the energy of the incident particle is such that the total energy is equal to a proper energy of the complex. When the level width is greater than the spacing these effects will disappear, but the behaviour will not correspond to classical conditions unless the wave-length of the incident particle is also short compared with the effective dimensions R of the complex.

A further interesting feature of collisions in which the formation of a complex occurs is that the chance of emission of the surplus energy as radiation may be quite high. Under the circumstances we have previously assumed that the collision is over in such a short time that the chance of radiation during it is very small. Formation of a collision complex may hold the particles together for such a considerable time that they have a large chance of radiating energy. This chance may indeed become greater than that of re-emission of a particle (see Chap. XIII, § 2.22).

In nuclear collision phenomena all these effects occur.† Pronounced resonance is observed in the collisions of slow neutrons with nuclei, whereas in the case of fission of heavy nuclei by fast neutrons we have practically classical conditions. Chemical reactions between molecules, during which no electronic transitions occur, also provide examples which follow classical mechanics very closely. The concept of the collision complex has proved very fruitful in dealing with all these phenomena.

8.1. *The one-level formula*

We now derive, by a method due to Bethe,‡ the so-called one-level formula for collisions of a particle with a system of particles under conditions which lead to formation of a complex. The method is far from rigorous and relies to some extent on intuition, but has the advantage of following a procedure similar, in general, to that adopted in earlier sections of this chapter.

† The necessity for regarding nuclear collisions in terms of the collision complex was first pointed out by Bohr, *Nature*, **137** (1936), 344.

‡ *Rev. Mod. Phys.* **9** (1937), 101.

For simplicity we investigate the cross-section for a rearrangement collision in which a particle 1 is incident on a system A whose internal coordinates are denoted by \mathbf{r}_a , and a rearrangement occurs in which particle 1 is captured and a second particle 2 is emitted, leaving a system B whose internal coordinates are denoted by \mathbf{r}_b . We shall suppose further that neither the initial nor the final nucleus possesses angular momentum and that neither particle has any spin.

The Schrödinger equation for the system may be written either in the form

$$(\mathcal{H} - E)\Psi \equiv \left[-\frac{\hbar^2}{8\pi^2 M_1} \nabla_1^2 + H_a(\mathbf{r}_a) + V_1(\mathbf{r}_1, \mathbf{r}_a) - E \right] \Psi = 0, \quad (101)$$

where H_a is the Hamiltonian for the internal motion of system A , $V(\mathbf{r}_1, \mathbf{r}_a)$ is the interaction energy, \mathbf{r}_1 the relative coordinates, and M_1 the reduced mass of particle 1 and system A , or

$$(\mathcal{H} - E)\Psi \equiv \left[-\frac{\hbar^2}{8\pi^2 M_2} \nabla_2^2 + H_b(\mathbf{r}_b) + V_2(\mathbf{r}_2, \mathbf{r}_b) - E \right] \Psi = 0, \quad (102)$$

in terms of the internal coordinates \mathbf{r}_b of system B and the relative coordinates \mathbf{r}_2 of particle 2 and system B . Following the same procedure as in § 4.1, generalized to this case as in § 4.2, we have, without approximation,

$$(\nabla_1^2 + k_1^2)F(\mathbf{r}_1) = \frac{8\pi^2 M_1}{\hbar^2} \int \psi^*(\mathbf{r}_a) V_1(\mathbf{r}_1, \mathbf{r}_a) \Psi \, d\tau_a, \quad (103)$$

$$(\nabla_2^2 + k_2^2)G(\mathbf{r}_2) = \frac{8\pi^2 M_2}{\hbar^2} \int \phi^*(\mathbf{r}_b) V_2(\mathbf{r}_2, \mathbf{r}_b) \Psi \, d\tau_b, \quad (104)$$

ψ , ϕ being the respective wave functions for the initial state of system A and the final state of system B and

$$k_1^2 = \frac{8\pi^2 M_1}{\hbar^2} (E - E_a), \quad k_2^2 = \frac{8\pi^2 M_2}{\hbar^2} (E - E_b). \quad (105)$$

To proceed further it is necessary to introduce some approximation for Ψ on the right-hand side of (103) and (104). Previously we have taken

$$\Psi = F(\mathbf{r}_1)\psi(\mathbf{r}_a) + G(\mathbf{r}_2)\phi(\mathbf{r}_b), \quad (106)$$

but it is now essential to introduce a term representing the collision complex.

We suppose that there exists one non-degenerate energy-level E_c of the complex much closer to E than any of the others. The total angular momentum quantum number associated with this level we shall take to be l . If the polar axis is taken along the direction of the incident

particles, the z -component of the angular momentum must be zero. If $\chi_c(\mathbf{r}_a, \mathbf{r}_b)$ is the wave function of the complex in this state, we now write

$$\Psi = F(\mathbf{r}_1)\psi(\mathbf{r}_a) + G(\mathbf{r}_2)\phi(\mathbf{r}_b) + c\chi_c(\mathbf{r}_a, \mathbf{r}_b), \quad (107)$$

ignoring the effect of the other states of the complex. c is a constant to be determined.

Substitution in (103) and (104) gives

$$\begin{aligned} & (\nabla_1^2 + k_1^2 - U_1)F(\mathbf{r}_1) \\ &= cU_{1c}(r_1)P_l(\cos\theta_1) + \frac{8\pi^2 M_1}{\hbar^2} \int \psi^*(\mathbf{r}_a)V_1\phi(\mathbf{r}_b)G(\mathbf{r}_2) d\tau_a, \end{aligned} \quad (108)$$

$$\begin{aligned} & (\nabla_2^2 + k_2^2 - U_2)G(\mathbf{r}_2) \\ &= cU_{2c}(r_2)P_l(\cos\theta_2) + \frac{8\pi^2 M_2}{\hbar} \int \phi^*(\mathbf{r}_b)V_2\psi(\mathbf{r}_a)F(\mathbf{r}_1) d\tau_b, \end{aligned} \quad (109)$$

where

$$U_1 = \frac{8\pi^2 M_1}{\hbar^2} \int V_1 |\psi(\mathbf{r}_a)|^2 d\tau_a, \quad (110)$$

$$U_2 = \frac{8\pi^2 M_2}{\hbar^2} \int V_2 |\phi(\mathbf{r}_b)|^2 d\tau_b, \quad (111)$$

$$U_{1c}(r_1)P_l(\cos\theta_1) = \frac{8\pi^2 M_1}{\hbar^2} \int \psi^*(\mathbf{r}_a)V_1\chi_c d\tau_a, \quad (112)$$

$$U_{2c}(r_2)P_l(\cos\theta_2) = \frac{8\pi^2 M_2}{\hbar^2} \int \phi^*(\mathbf{r}_b)V_2\chi_c d\tau_b. \quad (113)$$

The angular dependence of the integrals (112), (113) follows from the angular momentum conditions we have assumed. As it is supposed that transitions take place almost exclusively through the complex, and not directly, we may ignore the last integrals in each of (108) and (109). To be consistent we must also suppose the function U_1 , which produces direct elastic scattering, to be small within the boundary of the collision complex. The same will apply to U_2 .

The solutions of (108) and (109) satisfying the boundary conditions may now be obtained by the method described in Chap. VI, § 3. We find

$$F(\mathbf{r}) = \sum_s i^s (2s+1) e^{i\eta_s} f_s(r) P_s(\cos\theta) - k_1 c u_{1c} \{i f_l(r) + h_l(r)\} P_l(\cos\theta), \quad (114)$$

where $f_s(r)$ is the solution of

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dL}{dr} \right) + \left\{ k_1^2 - U_1 - \frac{s(s+1)}{r^2} \right\} L = 0, \quad (115)$$

which is bounded at the origin and has the asymptotic form

$$f_s \sim (k_1 r)^{-1} \sin(k_1 r - \frac{1}{2}s\pi + \eta_s); \quad (116)$$

u_{1c} is given by
$$u_{1c} = \int_0^\infty U_{1c}(r) f_i(r) r^2 dr; \tag{117}$$

and the function $h_l(r)$ by

$$u_{1c} h_l(r) = f_l(r) \int_r^\infty U_{1c} f_l^i r'^2 dr' + f_l^i(r) \int_0^r U_{1c} f_l r'^2 dr', \tag{118}$$

where f_l^i is the second solution of (115) which has the asymptotic form

$$f_l^i \sim (k_1 r)^{-1} \cos(k_1 r - \frac{1}{2}l\pi + \eta_l).$$

It will be noted that as $r \rightarrow \infty$, $h_l(r) \rightarrow f_l^i(r)$.

In the expression (114) for $F(\mathbf{r})$ the first series represents the incident plane wave plus the wave scattered by the potential U_1 , the second series the contribution by re-emission from the collision complex. The differential cross-section for elastic scattering is then

$$I_{el}(\theta) = \left| \frac{1}{2ik} \sum_s (e^{2i\eta_s} - 1)(2s + 1) P_s(\cos \theta) - (-i)^l c e^{i\eta} u_{1c} P_l(\cos \theta) \right|^2. \tag{119}$$

In the same way we find

$$G(\mathbf{r}) = -k_2 c u_{2c} \{i g_l(r) + j_l(r)\} P_l(\cos \theta), \tag{120}$$

where the symbols follow the corresponding definitions to those for $F(\mathbf{r})$. In this case there is no incident wave. The differential cross-section for the rearrangement collision is

$$I_a(\theta) = \frac{M_1}{M_2} \frac{k_2}{k_1} |c|^2 |u_{2c}|^2 \{P_l(\cos \theta)\}^2. \tag{121}$$

It thus remains to determine c , which we choose so that

$$\iint \chi_c^* (\mathcal{H} - E) \Psi d\tau d\tau_a = 0, \tag{122}$$

with the approximation (107) substituted for Ψ .†

Since

$$\begin{aligned} (\mathcal{H} - E) \chi_c &\simeq (E_c - E) \chi_c, \\ \int \chi_c^* (\mathcal{H} - E) c \chi_c d\tau d\tau_a &\simeq c (E_c - E). \end{aligned} \tag{123}$$

For the contribution from $F\psi$ we have from (108)

$$\begin{aligned} (\mathcal{H} - E) F\psi &= \left\{ -\frac{\hbar^2}{8\pi^2 M_1} (\nabla_1^2 + k_1^2) + V_1(\mathbf{r}_1, \mathbf{r}_a) \right\} F\psi, \\ &= -\frac{\hbar^2}{8\pi^2 M_1} \{c U_{1c} P_l(\cos \theta_1) \psi + U_1 F\psi\} + V_1 F\psi. \end{aligned} \tag{124}$$

† See note on p. 178.

As explained earlier, U_1 is to be neglected within the boundary of the complex so that its overlap with χ_c is negligible. This leaves

$$\int \chi_c^*(\mathcal{H} - E)F\psi \, d\tau d\tau_a = -\frac{\hbar^2}{8\pi^2 M_1} c \int \chi_c^* U_{1c} P_1(\cos \theta_1) \psi \, d\tau d\tau_a + \int \chi_c^* V_1 F\psi \, d\tau d\tau_a. \quad (125)$$

We consider first the second integral. In view of (112) we have

$$\frac{8\pi^2 M_1}{\hbar^2} \int \chi_c^* V_1 \psi \, d\tau_a = U_{1c}^*(r_1) P_1(\cos \theta). \quad (126)$$

Substituting now, from (114), for F we find

$$\frac{8\pi^2 M_1}{\hbar^2} \int \chi_c^* V_1 F\psi \, d\tau d\tau_a = 4\pi \left[i e^{i\eta} u_{1c}^* - k_1 c \left(\frac{i|u_{1c}|^2}{2l+1} + s_1 \right) \right], \quad (127)$$

where s_1 , arising from h_1 in (118), is real. Returning to the first integral in (125) we shall be content with noting that it is also real and may be included in s_1 .

A similar discussion gives

$$\frac{8\pi^2 M_2}{\hbar^2} \int \chi_c^* V_2 G\phi \, d\tau d\tau_b = -4\pi k_2 c \left(\frac{i|u_{2c}|^2}{2l+1} + t_1 \right), \quad (128)$$

where t_1 is real.

Collecting the terms for substitution in (123) we have

$$c(E - E'_c + \frac{1}{2}i\Gamma_c) = \frac{\hbar^2}{2\pi M_1} i e^{i\eta} u_{1c}^*,$$

with
$$\Gamma_c = \frac{\hbar^2}{\pi} \left[\frac{k_1}{M_1} \frac{|u_{1c}|^2}{2l+1} + \frac{k_2}{M_2} \frac{|u_{2c}|^2}{2l+1} \right]. \quad (129)$$

E'_c is written in place of E_c to allow for the additional real terms involving c which appear in (127) and (128).

We now have for the cross-section for the rearrangement collision

$$Q_d = \frac{\pi}{k_1^2} (2l+1) \frac{\Gamma_1 \Gamma_2}{(E - E'_c)^2 + \frac{1}{4}(\Gamma_1 + \Gamma_2)^2}, \quad (130)$$

where
$$\Gamma_1 = \frac{k_1 \hbar^2}{\pi M_1} \frac{|u_{1c}|^2}{2l+1}, \quad \Gamma_2 = \frac{k_2 \hbar^2}{\pi M_2} \frac{|u_{2c}|^2}{2l+1}. \quad (131)$$

This is the so-called one-level formula, first derived by Breit and Wigner.†

8.11. Significance of the one-level formula. The formula (130) is of

† *Phys. Rev.* **51** (1937), 593.

typical resonance form with the total width at half maximum equal to $\Gamma_1 + \Gamma_2$. It may be compared with the corresponding optical formula for the breadth of a spectrum line.

Consider the resonance absorption of light by an atom which raises it from the ground state A to a state B from which it may drop either to the state A or to one intermediate state C . The line width of the resonance absorption is then given by $\Gamma_{AB} + \Gamma_{CB}$, where Γ_{AB}/\hbar and Γ_{BC}/\hbar are the transition probabilities from the state B to states A and C respectively. By analogy we may interpret Γ_1/\hbar , Γ_2/\hbar as giving the chance that, in unit time, particle 1 or particle 2 respectively will be emitted from the collision complex. This is consistent with the formulae (131), for u_{1c} , u_{2c} are determined by the overlap of the function χ_c representing the complex and the functions $F\psi$, $G\phi$ respectively, as usual in expressions for transition probabilities.

Adopting this viewpoint we must suppose that

$$\frac{\pi}{k_1^2} (2l+1) \frac{\Gamma_1(\Gamma_1 + \Gamma_2)}{(E - E'_c)^2 + \frac{1}{4}(\Gamma_1 + \Gamma_2)^2}$$

represents the cross-section for formation of the complex, $\Gamma_2/(\Gamma_1 + \Gamma_2)$ giving the chance that it will break up by emission of the particle 2. Γ_1 and Γ_2 are usually referred to as the partial widths for emission of particles 1 and 2 respectively, since the total width Γ ($= \Gamma_1 + \Gamma_2$) can be analysed into separate contributions from the two possible modes of break-up of the complex.

The small shift of the resonance maximum from E_c to E'_c is unimportant for most applications as the value of E_c is not in general predictable, and it matters little whether E_c or E'_c is determined from experiment.

8.12. Elastic scattering. We should expect that, for elastic scattering, the effect of the resonance level of the complex would be to introduce a cross-section differing from (130) by the replacement in the numerator of Γ_2 by Γ_1 . Actually the formula for this case is complicated by the presence of a contribution to the scattered amplitude due to 'potential' scattering, arising partly before penetration of the nucleus and partly from 'shadow' diffraction round the nucleus (see this chapter, § 1). The partial elastic cross-section of order l becomes

$$Q_{el}^l = \frac{\pi}{k_1^2} (2l+1) \left| e^{2i\eta_l} - 1 + \frac{i\Gamma_1 e^{2i\eta_l}}{(E'_c - E) - \frac{1}{2}i(\Gamma_1 + \Gamma_2)} \right|^2. \quad (132)$$

There is some difficulty in providing a precise definition of the phase η_l which determines the potential scattering. We have defined it in

terms of the l th order wave equation for motion in the field of potential $\hbar^2 U/2M_1$, the interaction of particles 1 with the system A averaged over the initial wave function of that nucleus. For distances r greater than the radius R of the collision complex this can be accepted without objection but, for smaller distances, we must take account of the fact that the incident particle loses its identity in the formation of the complex. The chance that, on entering the system A , it is scattered directly without energy interchange is negligible. It is therefore natural to expect that, at $r = R$, the interaction $\hbar^2 U/2M_1$ is best represented as corresponding to an impenetrable sphere of radius R . Thus, in considering the impact of a particle of charge $Z_1 \epsilon$ with a nucleus of charge $Z_2 \epsilon$ we would take, in calculating η_l ,

$$\begin{aligned} \frac{\hbar^2}{2M_1} U_1 &= \frac{Z_1 Z_2 \epsilon^2}{r} \quad (r > R), \\ &\rightarrow \infty \quad (r = R). \end{aligned} \quad (133)$$

Further justification for this viewpoint will be given in § 8.2 below.† Unfortunately, in actual cases some ambiguity still remains in the choice of R .

8.13. Case when the complex may break up in more than two ways. We have derived the above formulae on the assumption that either one of only two particles can be emitted from the collision complex. It is an immediate generalization to give the formula when any one of n particles may be emitted. In place of (130) we have, for emission of the p th particle, a cross-section

$$\frac{\pi}{k^2} (2l+1) \frac{\Gamma_1 \Gamma_p}{(E - E'_c)^2 + \frac{1}{4} \left(\sum_1^n \Gamma_i \right)^2}, \quad (134)$$

with a corresponding modification of (132).

8.14. One-level formula with unrestricted angular momenta. The appropriate generalization of the one-level formula for the case when the incident particle has a spin of i quantum units and the struck system an angular momentum of s units has been given by Bethe and Placzek.‡ They obtain, in place of (130),

$$Q_d^2 = \frac{\pi}{k^2} \frac{2J+1}{(2i+1)(2s+1)} \frac{\Gamma_1 \Gamma_p}{(E - E'_c)^2 + \frac{1}{4} \Gamma^2}, \quad (135)$$

where J is the angular momentum quantum number of the complex.

† Bethe (*Rev. Mod. Phys.* 9 (1937), 91) shows that it is only with the assumption of an effective repulsive potential within the nuclear radius that the contribution from distant resonance levels is unimportant.

‡ *Phys. Rev.* 51 (1937), 450.

8.2. Generalization to many resonance levels of the complex. Partial widths smaller than level separation

Before generalizing the formula (134) to take account of the existence of more than one energy-level of the collision complex we must distinguish two cases. As the excitation energy of the complex increases the level separation will decrease (see Chap. XIII, § 2.1), so that eventually the level width will exceed the level spacing. We first discuss the case in which the excitation is not too high, so the levels do not overlap.

Bethe and Placzek† have given as the generalizations of (130) and (132) for this case

$$Q_a^l = \frac{\pi}{k^2} (2l+1) \left| \sum_r \frac{w_{1c}^r w_{pc}^{r*}}{(E'_{cr} - E) - \frac{1}{2}i \sum_t \Gamma_{tc}^r} \right|^2, \quad (136)$$

$$Q_{el}^l = \frac{\pi}{k^2} (2l+1) \left| e^{2i\eta_l} - 1 + i e^{2i\eta_l} \sum_r \frac{\Gamma_1^r}{(E'_{cr} - E) - \frac{1}{2}i \sum_t \Gamma_{tc}^r} \right|^2, \quad (137)$$

in which the separate states of the compound system are distinguished by the index r and $|w_{pc}^r|^2 = \Gamma_{pc}^r$.

These formulae were obtained by an extension of the method used in deriving the one-level formula. This derivation leaves much to be desired from the point of view of rigour. The compound state is only vaguely defined, and the wave function of the relative motion of an incident or outgoing particle within the complex is described only in an intuitive way. This leads to difficulty in determining the potential scattering and the matrix elements which define the partial level widths. A more rigorous treatment has been given by Kapur and Peierls‡ which avoids these difficulties.

8.21. Generalization of the one-body dispersion formula. Kapur and Peierls derived a many-body dispersion formula, which reduces to the Bethe-Placzek expression (135) when the partial widths are smaller than the level spacing, by generalizing the one-body formula given in Chap. II, § 7.

The first step is to introduce a precise definition of the compound system. Once again we choose a definite radius R for this system such that the chance of finding more than one particle of the system at a distance from the centre greater than R is small.

† *Rev. Mod. Phys.* **9** (1937), 106.

‡ *Proc. Roy. Soc. A*, **166** (1938), 166. See also Wigner, *Phys. Rev.* **70** (1946), 15; **70** (1946), 606; Wigner and Eisenbud, *ibid.* **72** (1947), 29; Feshbach, Peaslee, and Weisskopf, *ibid.* **71** (1947), 145.

Let Ψ be, as usual, the wave function for the complete system. We may expand Ψ in the form

$$\Psi = \sum \psi_n(\mathbf{r}_a) F_n(\mathbf{r}_1), \quad (138)$$

where the coordinates \mathbf{r}_1 refer to the relative motion of the incident particle and the centre of mass of the remainder. It is also possible, just as in § 8.1, to expand Ψ in any one of the alternative ways, such as

$$\Psi = \sum \phi_n(\mathbf{r}_b) G_n(\mathbf{r}_2), \quad (139)$$

in which \mathbf{r}_2 refers to the relative motion of a second particle and the centre of mass of the remainder. As this particle is not the incident one the functions G_n must represent outgoing waves only. Since for $r_2 < R$ the chance of finding two particles outside the system is small, we have

$$[\nabla^2 + k_2^2 - U_2(r_2)]G_n = 0 \quad (r_2 > R), \quad (140)$$

where U_2 includes only long-range interaction between the particle 2 and the residual system. Thus, if the collision is a nuclear one and the particle is charged, U_2 represents the Coulomb interaction. If we expand G_n in the usual way in a series of spherical harmonics

$$G_n = r_2^{-1} \sum g_n^l(r_2) P_l^m(\cos \theta_2) e^{\pm im\phi_2}, \quad (141)$$

the condition that G_n should represent outgoing waves only requires

$$\left(\frac{d}{dr_2} - f_{i2} \right) g_n^l = 0 \quad (r_2 = R), \quad (142)$$

where f_{i2} is as defined in Chap. II, § 7.†

A wave function χ_c^r , representing a stationary state of the compound system, is now defined so that, when expanded in any one of the alternative forms (138) or (139), the functions G_n , F_n satisfy the appropriate condition (142). By the inclusion of the function F_n for the incident particle the system is made a closed one, just as in the one-body case of Chap. II, § 7. Corresponding to each function χ_c^r there will be a complex energy value

$$W_r = E_r - \frac{1}{2}i\Gamma_r. \quad (143)$$

A procedure very similar to that employed in the one-body case may then be used to obtain an expansion of the wave function Ψ describing the collision in terms of the functions χ_c^r . This gives for the cross-sections Q_d^l and Q_{el}^l the formulae

$$Q_d^l = \frac{\pi}{k^2} (2l+1) \left| \sum_r \frac{\tilde{w}_{1c}^{r*} w_{pc}^r}{(E_r - E - \frac{1}{2}i\Gamma_r) N_r} \right|^2, \quad (144)$$

$$Q_{el}^l = \frac{\pi}{k^2} (2l+1) \left| e^{2i\eta_l} - 1 + ie^{2i\eta_l} \sum_r \frac{\tilde{w}_{1c}^{r*} w_{1c}^r}{(E_r - E - \frac{1}{2}i\Gamma_r) N_r} \right|^2. \quad (145)$$

† Or as in Chap. III, § 5.1, if a Coulomb field is present.

Here

$$\Gamma_r = \sum_p |w_{pc}^r|^2,$$

$$N_r = \int \tilde{\chi}_c^{r*} \chi_c^r d\tau_a d\tau_1, \quad (146)$$

where $\tilde{\chi}_c^{r*}$ differs from χ_c^r in that its expansions satisfy the conditions

$$\left(\frac{d}{dr_p} - f_{ip}^* \right) \tilde{g}_r^l = 0 \quad (r_p = R),$$

instead of (142), and $\int |\chi_c^r|^2 d\tau_a d\tau_1 = 1$. (147)

The quantities w_p receive in this treatment a precise significance. Thus

$$|w_{pc}^r|^2 = -(f_{ip}^r - f_{ip}^{r*}) |g_r^l(R)|^2 \frac{\hbar^2}{2M_p}, \quad (148)$$

and $|\tilde{w}_p^r|^2$ differs only in that $g_r^l(R)$ is replaced by $\tilde{g}_r^l(R)$. As it may be shown that $|g_r^l|^2 = |\tilde{g}_r^l|^2$, it follows that w_p^r differs from \tilde{w}_p^r only by a phase factor.

In the case of the cross-section for elastic scattering, the phase η_l is unambiguously determined when R is given. It represents the phase shift which would arise in the scattering by a potential which is of the form U_p for $r_p > R$ and presents an infinite barrier at $r_p = R$.

Comparison of the formulae (144), (145), which may be seen to be natural generalizations of the one-body formula (64) of Chap. II, with those (136), (137), given by Bethe and Placzek, reveals a close similarity. The main difference is in the inclusion of the factors N_r and the appearance of \tilde{w}_{pc}^r in place of w_{pc}^r . It has further been shown by Kapur and Peierls† that, when the spacing of the levels E_r is greater than their width Γ_r , these differences are unimportant. Apart from providing a rigorous justification for the use of the formulae (136) and (137) under these circumstances, the method of Kapur and Peierls has the advantage of giving definite expressions for the matrix elements w_{pc}^r and the potential scattering, provided the radius R of the compound system is fixed.

It must be remembered, however, that there remains ambiguity in the choice of R , just as in the one-body case. Referring to the expression (137) for the elastic scattering we can regard it as made up of three terms—the contribution from the nearest resonance level, that from the aggregate of all the more distant levels, and that from the potential scattering. The relative importance of the last two may be changed by a different choice of R . For convenience the best choice would be the

† Loc. cit.

one which minimized the contribution from the distant resonance levels. † As the theory has not so far developed to a stage in which it can be applied to prediction of cross-sections for particular cases, the practical problem of evaluating (137) has not yet arisen. It is of interest to note, however, that Breit ‡ has been able to introduce a schematic model of a dispersive reaction which permitted an exact algebraical treatment. The compound system appeared unambiguously in this analysis without any introduction of a range R .

8.22. *Variation of partial widths with velocity.* It will be noted that, in both the methods of Bethe and Placzek and of Kapur and Peierls, the energy-levels of the compound system depend on the energy of the incident particle. When the level width is small compared with the spacing, the dependence of the real part on this energy may be ignored as a small effect; but the contributions Γ_p^r from the partial level widths to the imaginary part $\frac{1}{2}i\Gamma_r$ depend quite strongly, in general, on the velocity of ejection of the particle concerned.

According to the formula of Kapur and Peierls §

$$\Gamma_p^r = |w_{pc}^r|^2, \quad (149)$$

where $|w_{pc}^r|$ is given by (148). Confining ourselves in the first instance to cases in which the potential acting on a particle when outside the system is zero we have, for particles of zero angular momentum,

$$f_0^r - f_0^{r*} = 2ik_p. \quad (150)$$

Γ_p^r is, therefore, proportional to the velocity of ejection under these circumstances.

If the particles have l units of angular momentum and $k_p R < l$, then

$$f_l^r - f_l^{r*} \propto k_p^{2l+1} R^{2l}, \quad (151)$$

and Γ_p^r is proportional to the $(2l+1)$ th power of the velocity.

These results would be expected also from the treatment given in § 8.1. The quantities u_{1c} , u_{2c} which occur there are determined mainly by the overlap of the functions f_i , g_i respectively with the region occupied by the compound system. For small values of kR the magnitude of the functions in this region will vary as $(kR)^l$ (see Chap. II, § 3.3), and hence u_{1c} , etc., will vary in the same way. As the corresponding widths are proportional to $k|u|^2$ they will vary as $k^{2l+1}R^{2l}$ in agreement with (151).

In view of the marked dependence of the partial width on energy the true width is often defined as the value at exact resonance.

† See footnote, p. 164.

‡ *Phys. Rev.* **69** (1946), 472.

§ *Loc. cit.*

If we now consider the effect of introducing a finite interaction U for $r > R$, the velocity variation of the partial widths becomes more complicated. The most important case in practice arises in nuclear collisions where U represents the Coulomb repulsion. The partial widths then contain the additional factor e^{-P_1} which gives the chance that the particle will penetrate the Coulomb potential barrier at the nuclear surface.†

A more detailed discussion of the application of the dispersion formula to nuclear collisions for the case of separated levels will be given in Chap. XIII, § 2.2. In § 8.31 below some further results of a statistical character concerning the energy variation of the widths will be given.

8.3. *The case of overlapping levels‡*

We now consider what can be done when the excitation energy of the complex is so high that the level widths are greater than the level separation and there is no longer a discrete spectrum. The formula (144) remains valid but is not in a suitable form for practical application. More convenient expressions may be obtained by statistical methods. Furthermore, when the wave-length of the particles emitted is also short compared with the dimensions of the complex a completely classical description is possible.

The one-level formula (134) expresses the fact that the ratio of the cross-sections Q_2^l, Q_3^l , etc., for different rearrangements involving, respectively, emission of particles 2, 3, etc., is independent of the way the compound system is formed, viz.

$$Q_2^l/Q_3^l = \Gamma_2/\Gamma_3, \text{ etc.} \tag{152}$$

According to it the total cross-section for all types of collision of particles 1 with the initial system, integrated over a range of energies including the resonance level, is given by

$$\int Q_{\text{tot}}^l dE = \frac{2\pi^2}{k^2} (2l+1)\Gamma_1, \tag{153}$$

provided the potential scattering is ignored. The average total cross-section for an energy interval containing many levels will therefore be

$$\bar{Q}_{\text{tot}} = \frac{2\pi^2}{k^2} (2l+1)\Gamma_1/D, \tag{154}$$

† See Chap. III, § 5.

‡ The discussion in this section follows closely that given by Bohr, Peierls, and Placzek, *Nature*, **144** (1939), 200, and other references to discussion of statistical applications include Bethe, *Rev. Mod. Phys.* **9** (1937), 96; Weisskopf, *Phys. Rev.* **52** (1937), 295.

where D is the mean energy separation of the levels in the interval concerned.

On the basis of these results we might expect, for the case of overlapping levels, that (154) would give the cross-section for formation of the complex and that (152) would then determine the chance that it would break up in any particular way. Thus we would have for the cross-section for a rearrangement in which particle 2 is emitted

$$Q_2^l = \frac{2\pi^2}{k^2} (2l+1) \frac{\Gamma_1 \Gamma_2}{D\Gamma}, \quad (155)$$

where

$$\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3 + \dots$$

We shall now show that a formula of this type may indeed be used, provided there is some reinterpretation of the significance of the quantities $\Gamma_1, \Gamma_2, \dots$, etc.

The first point is that in this case of overlapping levels the state of the complex is not defined by its energy alone. The wave function representing the complex will be a linear combination of functions for the separate levels which overlap at the particular energy concerned, and the coefficients in this combination will depend on the way the complex was formed. However, (155) may still be retained if $\Gamma_2, \Gamma_3, \dots$, etc., are associated with a definite mode of forming the complex, so that

$$Q_2/Q_3 = \Gamma_2^{(1)}/\Gamma_3^{(1)}, \quad (156)$$

the index 1 indicating that the complex has been formed by capture of the particles 1.

To derive the appropriate form of (154) we may apply the principle of detailed balancing to the reaction:

Particle 1 + system N in normal state \rightleftharpoons Complex,

in which the total energy lies between E and $E+dE$, supposed to be taking place within a volume V . Then, if p_1^c, p_c^1 are the respective probabilities of formation and disintegration of the complex per second,

$$g_c p_c^1 = g_N g_1 p_1^c, \dagger \quad (157)$$

where g_1, g_N, g_c are the statistical weights of the particle 1, system N , and complex c in the states concerned.

In the cases already considered, in which the particle 1 and system N have no spin and the total angular momentum quantum number of the complex is l ,

$$g_1 = \frac{V}{2\pi^2} k^2 dk, \quad g_N = 1, \quad g_c = (2l+1)Z, \quad (158)$$

† Fowler, *Statistical Mechanics*, 2nd edition, Cambridge (1936), p. 677.

where Z is the number of levels of the complex with suitable angular momentum and parity, lying in the interval E to $E+dE$, and k is the wave number of the relative motion of particle 1 and the system N .

In terms of our previous notation

$$p_1^c = \frac{v}{V} Q_{\text{tot}}^l, \quad p_c^1 = \Gamma_1^0/\hbar, \tag{159}$$

where v is the relative velocity of the particles 1 and systems N . Γ_1^0 is now the width of the compound state due to emission of particles 1, averaged over a statistical ensemble of complexes formed in all possible ways. We now have, since

$$\begin{aligned} \frac{dE}{dk} &= \hbar v, \\ Q_{\text{tot}}^l &= \frac{2\pi^2}{k^2} (2l+1)\Gamma_1^0 Z/dE \\ &= \frac{2\pi^2}{k^2} (2l+1)\Gamma_1^0/D. \end{aligned} \tag{160}$$

For practical purposes the modifications involved in (156) and (160) are usually unimportant.

8.31. *Statistical formula for level widths. The sticking probability.* The formula (160) may be used to obtain information about the order of magnitude of level widths considered as statistical average values.

The maximum value which Q_{tot}^l can have is $\pi(2l+1)/k^2$, so we may write

$$Q_{\text{tot}}^l = \frac{\pi}{k^2} (2l+1)\zeta_l, \tag{161}$$

where ζ_l is ≤ 1 . This gives

$$\sum (2l+1)\Gamma_1^0 = \frac{D}{2\pi} \sum (2l+1)\zeta_l. \tag{162}$$

Those emitted particles 1 which have an angular momentum such that $l > kR$ will contribute a negligible amount to the sum. Hence when kR is large

$$\sum (2l+1)\Gamma_1^0 = \frac{1}{2} Dk^2 R^2 \bar{\zeta}. \tag{163}$$

$\bar{\zeta}$, a mean value for ζ , is such that the cross-section for complex formation is $\pi R^2 \bar{\zeta}$. Since πR^2 is the geometrical cross-section, $\bar{\zeta}$ is usually called the 'sticking' probability. Introducing a mean value for Γ_1^0 also, we have

$$\bar{\Gamma}_1^0 = D\bar{\zeta}/2\pi. \tag{164}$$

The behaviour of the sticking probability as a function of energy has

† The level spacing D is now taken to be an average over all important angular momenta of the complex.

been investigated by Bethe.† In forming a complex the incident particle loses its identity and may be regarded as absorbed. As shown in Chap. I, § 7, absorption may be represented by the addition of a negative imaginary term to the potential energy. Bethe therefore discussed the motion of a particle under the action of a potential $V(r) - i\sigma(r)$, where $\sigma(r)$ represents an absorption potential. He found, as would be expected, that the sticking probability ζ tends to unity as the energy of the particle increases. On the other hand, the level separation decreases with the degree of excitation of the complex.‡ It follows from (164) that the level width, and hence the disintegration probability associated with emission of a particle of particular energy, eventually decreases as the energy increases beyond a certain value. In particular the chance that an incident particle will be re-emitted with its initial energy (elastic scattering) becomes very small at high energies of impact, as might be expected.

The total cross-section for a collision in which a particle 1, of high energy, is captured and particle 2 emitted, may now be written,

$$\begin{aligned} Q_1^2 &= \frac{\pi}{k^2} \sum_0^{kR} (2l+1) \Gamma_1^0 \frac{2\pi}{D} \frac{\Gamma_2^{(1)}}{\Gamma} \\ &= \pi R^2 \Gamma_2^{(1)} / \Gamma. \end{aligned} \quad (165)$$

This simple result expresses the fact that Q_1^2 is, in this case, equal to the geometrical cross-section of the system times the chance that the complex will decay by emission of the particular particle 2.

8.32. Energy distribution of the emitted particles. A highly excited complex may decay in stages by emitting a series of particles of considerably smaller energy than that of the incident one. The relative probability of emission of a particle leaving the complex in a particular energy state n is given by

$$\Gamma_{2(n)} = D \zeta_{2(n)} / 2\pi, \quad (166)$$

where D is the mean level distance in the excited complex and $\zeta_{2(n)}$ is the sticking probability which would be associated with an impact of the particle 2, possessing the same energy E as that with which it is emitted, with the residual system in state n . The chance $p_2(E)$ of emitting a particle 2 with energy between E and $E+dE$ will be proportional to $\Gamma_{2(n)}$ and to the number $\rho(E) dE$ of energy states of the final system which lie within a range dE about the state n . Thus

$$p_2(E) \propto \rho(E) \zeta_{2(n)}. \quad (167)$$

† *Phys. Rev.* **57** (1940), 1125.

‡ See Chap. XIII, § 2.1.

The density of energy-levels of the residual system increases rapidly with its degree of excitation, i.e. with decrease of E . On the other hand, $\zeta_{2(n)}$ falls off rather slowly as E decreases. The resulting distribution is therefore of the form shown in Fig. 20, with a maximum at a relatively low energy.

8.4. The transition state method

We discuss now a statistical method, first introduced by Pelzer and Wigner,[†] which may be employed in dealing with rearrangement reactions in which the conditions are entirely classical. It is particularly suited for the discussion of the rates of chemical reactions, but it may also be applied to nuclear phenomena, such as fission or fast neutron reactions, for which classical mechanics is valid.

A detailed picture of the course of the collision is then possible in principle and the transition state method makes use of this. Essentially it provides formulae for the statistical averages of the partial widths Γ_p of the different possible reactions. For chemical phenomena it is convenient to consider a macrocanonical ensemble of reactants as the observed reaction rates refer to such conditions. In nuclear applications a microcanonical ensemble is more appropriate.

We consider a reaction involving n 'particles'. They may be nucleons or atoms (it must be assumed in applying the method to atoms that, during the reaction, no electronic transitions take place). This system may be specified by $3n$ coordinates. Of these, three determine the position of the centre of mass and three the orientation of the whole, leaving $3n-6$ to describe the internal configuration. We may therefore think of a hypersurface representing the potential energy as a function of these $3n-6$ coordinates. This surface will include regions or basins of relatively low potential energy, separated by mountain ranges. These low-level basins correspond to separated reactants. In order to pass from one such basin to another, i.e. for a rearrangement to occur, the representative point must pass over the mountain range. To do this it will, in general, pass at the lowest point in the range. At this point the

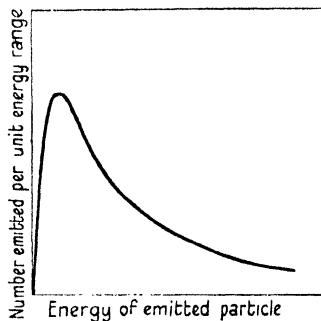


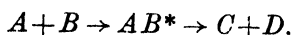
FIG. 20. Illustrating the energy distribution of particles emitted from a highly excited complex.

[†] *Z. physik. Chem. B*, 15 (1932), 445. For detailed discussion of the method see Wigner, *Trans. Far. Soc.* 34 (1938), 29; Glasstone, Laidler, and Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York (1944), Chaps. I, III, and IV.

potential energy will be a maximum for changes involving passage across the range, but will be a minimum for changes in perpendicular directions; in other words, the point is a col or saddle point in the surface. When the configuration of reactants is represented by this point, which is called the activation point, and is in such a state of motion as to pass from the initial low-level region across the range, it is said to be in the transition state, and to form an activated complex.

In most cases this represents an oversimplified picture. The passage from one low-level basin to the other may proceed through one or more high-level basins of complicated shape. Thus the representative point may enter such a basin through a narrow pass and may leave through a second such pass. In between it may execute a complicated series of motions depending on the shape of the basin. As a result of these it may be much more likely to return through the pass of entry than to proceed out through the other into the second low-level basin. The state of affairs is here rather like that in the collision complex already considered. Owing to the complicated shape of the high-level basin the system spends a long time there before sufficient energy concentrates on a mode of motion which takes the representative point out of the basin through one or other exit.

We now suppose the original reactants, and also those in the transition state, to be in statistical equilibrium at temperature T . It is usually unnecessary to consider reactions of higher order than the second, so we consider a reaction such as



AB^* represents the transition state. It may be considered as an ordinary molecule produced by association of the atoms A and B except that motion in one of the $3n-6$ coordinates specifying it will lead to decomposition. Applying then the usual statistical theory, the equilibrium concentration of activated complexes is given by†

$$N_{AB}^* = N_A N_B \frac{f_{AB}^*(T)}{f_A(T) f_B(T)}, \quad (168)$$

where N_A , N_B , f_A , f_B are the respective concentrations and partition functions of the systems A and B .

$f_{AB}^*(T)$ is the partition function of the transition state, and it may be written as follows. We suppose the coordinates chosen so that motion across the pass involves change in one coordinate q^* with corresponding

† Fowler, *Statistical Mechanics*, 2nd edition, Cambridge (1936), p. 160.

momentum p^* . In phase space the representative point must lie in the range $h^{-1} dp^* dq^*$, the other coordinates and momenta having any values consistent with these. It will normally be a good approximation to treat the motion in q^* as a pure translation and to factorize $f_{AB}(T)$ in the form

$$e^{-E^*/kT} dp^* dq^*/h, \quad (169)$$

where the first factor represents the contribution from all coordinates but q^* , the others that from q^* . E^* is the energy in this coordinate and is $\geq E_0$, the height of the pass.

The rate at which representative points cross the pass per second is given by $N_A N_B v^*/dq^*$, where v^* , its velocity along the reaction coordinate q^* , is given by p^*/m^* , m^* being the effective mass for this motion. Hence the total number of crossings per second in a volume V is

$$N_A N_B \frac{f^*(T)}{f_A(T) f_B(T)} \int_0^\infty e^{-E^*/kT} \frac{p^* dp^*}{m^* h}. \quad (170)$$

Writing $E^* = E_0 + p^{*2}/2m^*$, this gives

$$N_A N_B \frac{f^*(T)}{f_A(T) f_B(T)} \frac{kT}{h} e^{-E_0/kT}. \quad (171)$$

It is important to realize that (171) is not necessarily the rate of reaction. Thus, in the case in which a high-level basin exists, (171) merely gives the rate of entry to this basin. To obtain the rate of reaction we must multiply by a factor κ , usually called the transmission coefficient, which gives the chance that, once the representative point enters the high-level basin, it will escape by the pass leading to the particular resultants concerned, i.e. to $C+D$. In terms of the nomenclature of the preceding sections, the representative point in the high-level basin corresponds to the collision complex, the formula (171) is related to the sticking probability, and the transmission coefficient to the ratio Γ_{CD}/Γ which gives the chance that the complex will dissociate in a particular way. However, the applicability of the transition state method does not depend on the existence of an intermediate quasi-stationary state of relatively long life time.

To relate the formula (171) to the more usual one involving a collision cross-section, we first note that, if \bar{Q} is the cross-section for the rearrangement, averaged over the energy distribution, and E_0/kT is small, then the rate of reaction is given by

$$N_A N_B \bar{Q} \left(\frac{8kT}{m\pi} \right)^{\frac{1}{2}} e^{-E_0/kT}, \quad (172)$$

where m is the reduced mass. Hence

$$\bar{Q} = \kappa \left(\frac{\pi m k T}{8 h^2} \right)^{\frac{1}{2}} \frac{f^*(T)}{f_A(T) f_B(T)}. \quad (173)$$

In the simple case of a reaction between atoms A and B of masses m_1 , m_2 respectively, then

$$\begin{aligned} f_A(T) &= (2\pi m_1 k T)^{\frac{3}{2}} / h^3, & f_B(T) &= (2\pi m_2 k T)^{\frac{3}{2}} / h^3, \\ f^*(T) &= \{2\pi(m_1 + m_2)kT\}^{\frac{3}{2}} (8\pi^2 I k T / h^5), \end{aligned} \quad (174)$$

where I , the moment of inertia of the activated complex about its central axis, is given by

$$I = \frac{m_1 m_2}{m_1 + m_2} d_{12}^2,$$

d_{12} being the distance apart of the atoms in the activated state. We have then

$$\bar{Q} = \pi \kappa d_{12}^2. \quad (175)$$

We now illustrate the use of the method for discussing the behaviour of a microcanonical ensemble of systems with excitation energy between E and $E + dE$.† These systems may be atomic nuclei or activated molecules which, when left to themselves, will break up with release of the excess energy. If the number of systems in the ensemble is chosen to be equal to the number $\rho(E) dE$ of levels in the range E to $E + dE$, the number which break up per second will be $\rho(E) dE \Gamma / h$, Γ , having the same significance as in § 8.3. (159).

With the same notation as above, the number of levels in a distance dq^* , measured along the reaction coordinate in the transition state, will be

$$\rho^*(E - E^*) dE dp^* dq^* / h. \quad (176)$$

In the initial state there is one system in each of these levels, so the number which break up per second is

$$dE \int \frac{p^*}{m^*} \rho^*(E - E^*) \frac{dp^*}{h}. \quad (177)$$

Writing, as in (171), $E^* = E_0 + p^{*2} / 2m^*$, this becomes

$$\frac{dE}{h} \int \rho^*(E - E_0 - E_k) dE_k. \quad (178)$$

The integral is equal to the number N^* of levels in the transition state available with the given excitation. We therefore have

$$\begin{aligned} \rho(E) dE \Gamma / h &= dE N^* / h, \\ \Gamma &= N^* / \{2\pi \rho(E)\} \\ &= DN^* / 2\pi, \end{aligned} \quad (179)$$

† Bohr and Wheeler, *Phys. Rev.* **56** (1939), 426.

where D is the level separation in the excited system. An application of this result to the discussion of nuclear fission† will be made in Chap. XIII, § 6.3.

9. Summary of methods

A convenient way of summarizing the methods available for the discussion of inelastic collision probabilities is by means of the following table.

TABLE I

Conditions defining collision			Method available	Examples
Relative velocity	Magnitude of matrix elements of the interaction energy			
	Diagonal elements (V_{nn})	Non-diagonal elements (V_{on})		
Great compared with that of internal motions.	Any magnitude.	Any magnitude.	Born's approximation.	Collision of fast electrons with atoms.
Less than or comparable with that of internal motions.	Small.	Small.	Born's approximation.	
„ „	Large.	Small.	Method of distorted waves.	Excitation of molecular vibration by impact of atoms.
„ „	Any magnitude.	All small except V_{on} where 0th and n th states are in approximate resonance.	Solution of simultaneous equations.	Transfer of electronic excitation or charge.
„ „	Comparable and not small, but rates of change small throughout		Method of perturbed stationary state wavefunctions.	Excitation and ionization by slow positive ions.
„ „	Many large and with large rates of change.		Method of collision complex.	Nuclear collisions.

10. Collisions between two systems, one of which is initially at rest

In several sections of this book (Chap. V, § 3; Chap. VIII, §§ 2, 3, 4; Chap. XV, § 3) we have found the differential cross-section, $I(\theta) d\omega$,

† Ibid.

for collisions between two particles in which their centre of gravity is at rest. This is found by solving the equation

$$\nabla^2\psi + (8\pi^2m/\hbar^2)(\frac{1}{2}mv^2 - V)\psi = 0,$$

where m is the 'reduced mass', $m_1 m_2 / (m_1 + m_2)$, of the two particles, and v their relative velocity. If a solution is found of the form

$$\psi \sim e^{ikz} + r^{-1}e^{ikrf}(\theta),$$

then $I(\theta) = |f(\theta)|^2$. We show in this section how to find the differential cross-section when one particle, m_1 , is initially at rest. Denoting by $J(\Theta) d\Omega$ the differential cross-section in this case for scattering through an angle Θ into the solid angle $d\Omega$, we have

$$J(\Theta)\sin\Theta = I(\theta)\sin\theta d\theta/d\Theta,$$

where $\tan\Theta = m_1 \sin\theta / (m_1 \cos\theta + m_2)$.

In the special case where the masses are equal, $\Theta = \frac{1}{2}\theta$, and hence (unless the two particles are similar, cf. Chap. V, eq. (26))

$$J(\Theta) = I(2\Theta)4 \cos\Theta.$$

Footnote to page 161

This may be justified as follows. Suppose that the orthonormal set of functions χ_n are solutions of the equation

$$(H' - E_n)\chi_n = 0,$$

in which the Hamiltonian H' differs from \mathcal{H} by a small term H_1 . Substituting

$$\Psi = \sum a_n \chi_n$$

in the equation

$$(\mathcal{H} - E)\Psi = 0,$$

we find

$$\sum a_n (E_n - E)\chi_n = H_1 \Psi.$$

Multiplying by χ_n^* and integrating, this gives now

$$a_n = \int \chi_n^* H_1 \Psi d\tau d\tau_a / (E_n - E).$$

Formally this is equivalent to the condition

$$\int \chi_n^* (\mathcal{H} - E)\Psi d\tau d\tau_a = 0,$$

which is the more convenient form to use when an approximate form is taken for Ψ and H_1 is unknown.

IX

THE COLLISIONS OF FAST ELECTRONS WITH ATOMS. ELASTIC SCATTERING—BORN'S APPROXIMATION

1. Introductory. The experimental methods and results†

IN this chapter, and in Chapters X, XI, XII, and XIII, we apply the general theory of Chapter VIII to the detailed investigation of particular problems. Of these the most important are those associated with the collisions of electrons with atoms. The results of the calculations are expressed in terms of the differential and total cross-sections corresponding to collisions in which the n th state of the atom is excited by electrons of definite velocity v . These will be denoted by $I_n(\theta)$ and Q_n respectively,‡ and are such that

$$2\pi \int_0^\pi I_n(\theta) \sin \theta \, d\theta = Q_n. \quad (1)$$

For the case of the excitation of continuous energy-levels, a level is defined by a quantity κ such that the energy corresponding to the level is given by

$$E_\kappa = \kappa^2 \hbar^2 / 8\pi^2 m. \quad (2)$$

The cross-section corresponding to excitation of a set of levels between κ and $\kappa + d\kappa$ is then denoted by $Q_\kappa d\kappa$.

The differential cross-section determines the angular distribution of the scattered electrons, whereas the total cross-section determines the total probability of excitation of the given state.

As it is of importance to keep the theory in close relation to the practical side of the subject, we will first outline the different types of experimental investigation concerned with the collisions of electrons with atoms, and indicate the relations of the observed quantities to the calculated differential and total cross-sections. The types of experiment may be classified as follows:

1.1. *Experiments in which the aggregate of effects due to all types of collision, elastic and inelastic, are observed*

The results of these experiments give information only about the Q 's, not the differential cross-sections, and do not usually distinguish

† For a detailed account see Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chaps. I and II.

‡ Cf. Chap. II, § 1.

between the Q 's corresponding to different states. The two types of experiment falling under this head are as follows:

(a) *Measurements of the stopping-power of matter for fast electrons.* Here the experimental methods consist in the investigation of the ranges of fast particles in different materials. The stopping-power is defined in terms of the loss of kinetic energy of the electron per cm. of path in the material. Denoting the energies of the bound atomic states by E_n , we see that this rate of loss of kinetic energy is given by

$$-\frac{dT}{dx} = N \left\{ \sum_n Q_n (E_n - E_0) + \int_{\kappa=0}^{\kappa_{\max}} (E_\kappa - E_0) Q_\kappa d\kappa \right\}, \quad (3)$$

where E_0 is the energy of the normal state of the atom, and E_κ is given by (2). N is the number of atoms per c.c. of the material, and κ_{\max} is related by formula (2) to the maximum energy which the electron can give to the atom.

In certain cases the methods used may be applied to obtain information about individual collisions; the calculation of the stopping-power in terms of this summation is, however, of importance, in view of the application of range measurements to determinations of the initial energy of the particle.†

(b) *Measurement of total cross-sections.* If a homogeneous beam of electrons is fired through a gas, the beam becomes diffuse, and, if its initial energy is greater than the resonance potential of the gas, it will also become inhomogeneous.

Let J be the intensity of the electron beam. Then, if we regard every electron which is deviated or loses energy on collision as lost from the beam, the loss of intensity $|\delta J|$ in traversing a distance δx in the gas at pressure p may be written in the form

$$\delta J = -Jap \delta x,$$

where a depends only on the nature of the gas and the energy of the electron beam. Integrating this equation, we obtain for the intensity in the beam after traversing a distance x cm.,

$$J = J_0 e^{-apx}.$$

By measuring the variation of the beam current with length of path in the gas the quantity a may be measured. This type of experiment was introduced by Ramsauer‡ and has been applied by him and by

† See, for example, Blackett and Occhialini, *Proc. Roy. Soc. A*, **139** (1933), 699.

‡ *Ann. der Physik*, **64** (1921), 513.

various other investigators to the measurement of a for all simple gases and some metallic and other vapours.†

From the definition of the cross-section Q it is clear that, if N is the number of atoms per c.c. in the gas at normal temperature and pressure,

$$a = \frac{Np'}{760} \left[\sum_n Q_n + \int_0^{\kappa_{\max}} Q_\kappa d\kappa \right],$$

where p' is the unit of pressure (actually 1 mm. Hg) in the units (mm. of mercury) adopted in the experimental determinations. If the cross-sections Q_n , $Q_\kappa d\kappa$ are measured in units of πa_0^2 , where a_0 is the radius of the first Bohr orbit in hydrogen, we have, for this pressure

$$a = 3 \cdot 15 \left[\sum_n Q_n + \int_0^{\kappa_{\max}} Q_\kappa d\kappa \right].$$

The application of this method, unlike that of the stopping-power investigations, is restricted to electrons of slow to medium velocities‡ (0.5 to 400 volts), and it is seen from the above that it gives only the magnitude of the sums of all cross-sections. For electrons with energies below the resonance potential of the gas, however, only the elastic cross-section Q_0 will be effective; and so in this range of energies the method gives results of especial significance.

It is of interest to point out here that the experimental definition of a given above would be meaningless on the classical theory unless the colliding systems had definite boundaries, and the observed values would depend on the actual definition of a collision provided by the dimensions of the receiving slits of the apparatus. This difficulty does not occur on the quantum theory, as the cross-sections Q are definite, provided that the field of force of the scatterer falls off sufficiently rapidly with distance, a condition satisfied by all atomic fields. This point is discussed in Chapter II, end of § 1, and experimental evidence in its favour is described in Chap. X, § 1.

In connexion with this type of experiment we must also mention the method due to Townsend.§ The interpretation of the initial observations in this method requires the use of a complicated classical theory of the motion of electrons in gases, and its application is naturally

† See, for example, the summaries by Kollath, *Phys. Zeits.* **31** (1931), 985; Brode, *Rev. Mod. Phys.* **5** (1933), 258, and Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chap. I.

‡ Brode, *Phys. Rev.* **39** (1932), 547, has measured a for argon for electrons of energy up to 2,500 volts by a modification of the usual method.

§ *Phil. Mag.* **42** (1921), 873.

limited to conditions under which the theory holds, viz. at very low velocities of impact (below 5 volts in most gases). Inasmuch as this method gives information as to the form of Q_0 for much lower electron velocities than the method of Ramsauer, the results obtained by its use are of considerable importance.

1.2. *Experiments in which the different types of collision, elastic and inelastic, are investigated separately*

From the results of these investigations information is obtained about the relative magnitudes of the different cross-sections Q_n for a given incident velocity, and about the differential cross-sections $I_n(\theta)$ as functions of angle of scattering, and also about the variation of any one cross-section Q_n with velocity of impact. Absolute magnitudes are not usually measured, but these may be obtained from experiments of the first type.

For convenience of description these methods may be further divided into three classes:

(a) *Electrical methods.* In experiments of this type direct measurements are made of the angular distributions of scattered electrons or of the relative excitation probabilities, by observing the scattered currents. For the case of ionizing impacts, the absolute ionization cross-section $\int_0^{\kappa_{\max}} Q_{\kappa} d\kappa$ may be measured by observing the positive ion current produced by a homogeneous beam of electrons fired through a gas at low pressure.

(b) *Optical methods.* In this type of experiment a homogeneous electron beam is fired through a gas or vapour, and the intensity of the light of different wave-lengths emitted by atoms excited by the electron beam is measured. The intensity of light emitted, corresponding to a switch from a state n to a state m of a gas atom, will be proportional to

$$Q_n A_{nm},$$

where A_{nm} is the optical transition probability from state n to state m . The variation in the intensity of the light of a given wave-length with the velocity of the exciting electrons will then give the variation of Q_n with the velocity of impact, as A_{nm} is independent of the method of excitation. If A_{nm} can be calculated, it is also possible to compare the magnitudes of the cross-sections Q_n for different n .

This method has the advantage of being more sensitive than the electrical method; and thus the behaviour of the cross-sections Q_n may be examined for quite high excited states.

We thus see that the experimental material available is sufficiently diverse to provide ample illustration of the theory and to test its validity. Conversely, the theory is in a position to throw light on a large variety of phenomena of interest and importance to the physicist. Before proceeding to the detailed calculations of differential and total cross-sections we will consider briefly the order of treatment. We consider first elastic collisions, using the simplest formula, the first approximation of Born's theory, Chap. VII, § 1. The range of validity of this formula is examined and the theory then improved (Chap. X) by using the method of Faxén and Holtsmark given in Chapter II. We then introduce further improvements in certain cases, including a consideration of electron exchange. Up to this point the calculations require no mention of inelastic collisions, but in a more accurate theory one cannot discuss elastic conditions without discussing the inelastic at the same time, and the effect of the interaction of the inelastically scattered waves on the elastic is next briefly discussed. This, then, provides a convenient point (Chap. XI) for the detailed discussion of inelastic collisions. Just as for the elastic collisions, we begin with Born's first approximation (which is sufficient for the calculation of the stopping-power of matter for fast particles) and then consider the improvements necessary for slower particles.

2. Elastic scattering. Born's first approximation

It was shown in Chap. VII, § 1, that the differential elastic cross-section $I(\theta)$ for an elastic collision of an electron of velocity v with a spherically symmetrical field of force of potential $V(r)$ is given within the range of validity of Born's first approximation by†

$$I(\theta) = \left| \frac{8\pi^2 m}{h^2} \int_0^\infty \frac{\sin Kr}{Kr} V(r) r^2 dr \right|^2 \quad (K = 4\pi m v \sin \frac{1}{2}\theta/h). \quad (4)$$

A second formula showing the relation between (4) and the formula for the scattering of X-rays was also obtained.‡ We have now to calculate $I(\theta)$ when $V(r)$ is the field of an atom.

If $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$ is the wave function of the atom (atomic number Z), we have§

$$V(r) = -e^2 \int \left(\frac{Z}{r} - \sum_{n=1}^Z \frac{1}{|\mathbf{r} - \mathbf{r}_n|} \right) |\psi_0(\mathbf{r}_1, \dots)|^2 d\tau_1 \dots d\tau_Z. \quad (5)$$

As the wave function ψ_0 is only known analytically for a very few

† Cf. Chap. VII, eq. (12). ‡ Cf. Chap. VII, eq. (8). § Cf. Chap. VIII, §§ 2, 3.

atoms, the calculation of $V(r)$ for most atoms depends on the application of numerical methods; we will first consider the cases where ψ_0 is known analytically.

3. Scattering by hydrogen and helium

For hydrogen we have

$$\psi_0 = (\pi a_0^3)^{-\frac{1}{2}} e^{-r/a_0}. \quad (6)$$

For helium we may take with sufficient approximation the wave function obtained by Hylleraas† using a variation method, viz.

$$\psi_0 = (Z^3/\pi a_0^3)^2 e^{-Z(r_1+r_2)/a_0} \quad (Z = 1.69). \quad (7)$$

Substituting these expressions in (5) and integrating, we find

$$\begin{aligned} V(r) &= -\epsilon^2 \left(\frac{1}{r} + \frac{1}{a_0} \right) e^{-2r/a_0} \quad \text{for hydrogen,} \\ &= -2\epsilon^2 \left(\frac{1}{r} + \frac{Z}{a_0} \right) e^{-2Zr/a_0} \quad \text{for helium.} \end{aligned} \quad (8)$$

TABLE I

Scattered Intensities for Helium and Hydrogen

$\frac{ka_0}{Z} \sin \frac{1}{2}\theta$	$\frac{\sqrt{(\text{Volts})}}{Z} \sin \frac{1}{2}\theta$	$\{Z^4 I(\theta)/A\} \times 10^{18} \text{ cm.}^2$
0	0	27.9
0.03	0.11	27.9
0.05	0.18	27.7
0.10	0.37	27.1
0.20	0.74	24.8
0.30	1.11	21.6
0.40	1.48	18.0
0.50	1.85	14.5
0.60	2.21	11.4
0.70	2.58	8.78
0.80	2.95	6.73
0.90	3.32	5.14
1.00	3.69	3.93
1.20	4.43	2.33
1.40	5.17	1.43
1.60	5.91	0.904
1.80	6.64	0.593
2.00	7.38	0.402
2.50	9.23	0.172
3.00	11.1	0.084
3.50	12.9	0.046
4.00	14.8	0.027
4.50	16.6	0.017
5.00	18.5	0.011

$\left. \begin{matrix} Z = 1 \\ A = 1 \end{matrix} \right\}$ for hydrogen. $\left. \begin{matrix} Z = 1.69 \\ A = 4 \end{matrix} \right\}$ for helium.

† *Zeits. f. Physik*, 54 (1929), 347.

Substituting in the expression (4) for $I(\theta)$, we obtain, after an elementary integration,

$$I(\theta) = \frac{64\pi^4 m^2 \epsilon^4 A (2\lambda^2 + K^2)^2}{h^4 (\lambda^2 + K^2)^4}, \quad (9)$$

where for hydrogen $A = 1, \quad \lambda = 2/a_0,$

and for helium $A = 4, \quad \lambda = 3.36/a_0.$

By means of this formula the angular distributions of electrons elasti-

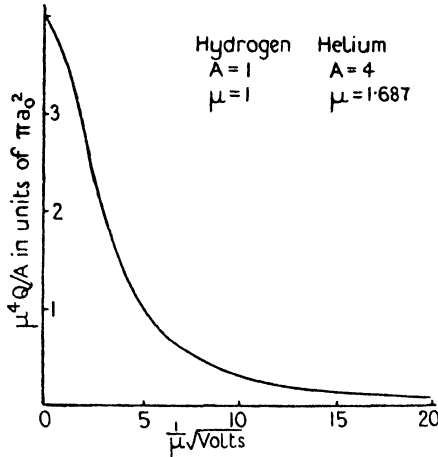


FIG. 21. Elastic cross-sections for hydrogen and helium.

cally scattered in hydrogen and helium may readily be calculated. In Table I $I(\theta)$ is tabulated as a function of $v \sin \frac{1}{2}\theta$ for these two atoms.

The total elastic cross-section Q_0 may now be calculated. We have

$$\begin{aligned} Q_0 &= 2\pi \int_0^\pi I(\theta) \sin \theta \, d\theta \\ &= \frac{1024 A \pi^5 m^2 \epsilon^4 (3\lambda^4 + 18\lambda^2 k^2 + 28k^4)}{3h^4 \lambda^2 (\lambda^2 + 4k^2)^3}. \end{aligned} \quad (10)$$

Q_0 is a monotonic function of $k = 2\pi m v/h$, as is clear from Fig. 21, where Q_0 is plotted against k .

3.1. Comparison with experiment

Measurements of the angular distributions of electrons scattered elastically by helium atoms have been carried out by a number of investigators,† for electrons with energies ranging from 1.8 to 700 volts.

† Dymond and Watson, *Proc. Roy. Soc. A*, **122** (1929), 571; McMillen, *Phys. Rev.* **36** (1930), 1034; Bullard and Massey, *Proc. Roy. Soc. A*, **133** (1931), 657; Ramsauer and

In Fig. 22 the experimental curves for electrons with energies greater than 50 volts are compared with those calculated from the formula (9) above. As the experiments are unable to furnish absolute values of the scattering, the scale has been adjusted so that the observed and calculated values of the scattering for 700-volt electrons agree.

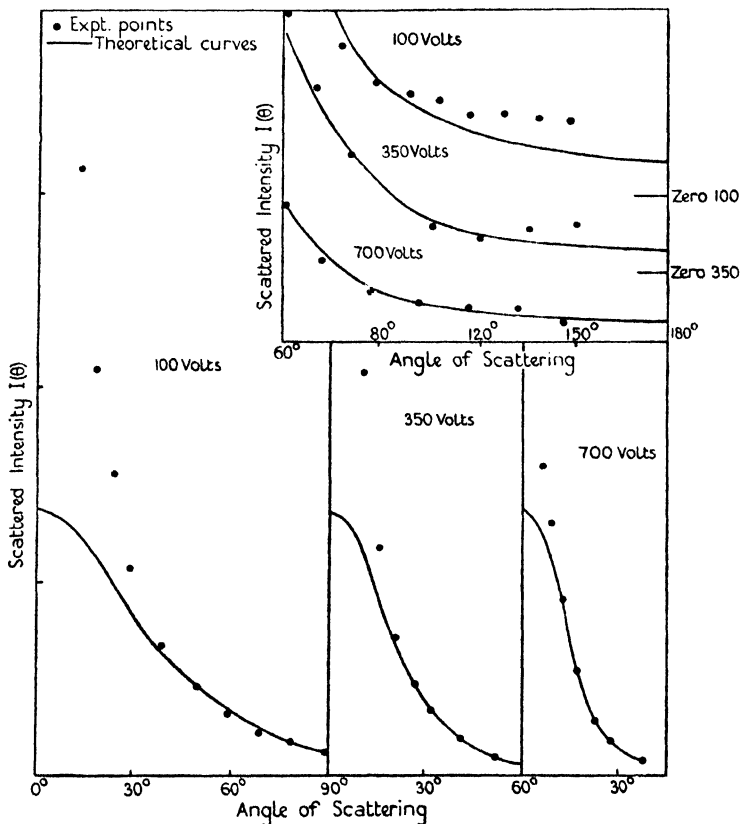


FIG. 22. Angular distributions of electrons scattered by helium atoms.

It is seen that the agreement then obtained at voltages above 100 volts is quite good over a large angular range. However, at both small and large angles of scattering noticeable discrepancies occur. Thus, for electrons with energies less than 500 volts the scattering becomes almost independent of angle at large angles of scattering instead of falling off uniformly with increase of angle (see inset figure). This behaviour is

Kollath, *Ann. der Phys.* **12** (1932), 529; Werner, *Proc. Roy. Soc. A*, **134** (1932), 202; Hughes, McMillen, and Webb, *Phys. Rev.* **41** (1932), 154; Mohr and Nicoll, *Proc. Roy. Soc. A*, **138** (1932), 229, 469.

explained in § 5 as due to the distortion of the incident wave by the atomic field.

At small angles of scattering the observed variation of intensity with angle is greater than the calculated. This seems to be due to polarization of the atom by the incident electron and will be further discussed in Chap. X, § 1.

For voltages less than 100 volts the agreement is unsatisfactory at all angles. The reasons for these deviations will be discussed in § 5 of this chapter and in §§ 4, 6, and 7 of Chapter X.

It thus appears that Born's formula (9) is approximately valid for electrons of energy greater than 100 volts, scattered by helium atoms, but it is not completely accurate over the whole angular range until the electron energy is as great as 500 volts.

4. The calculation of $I(\theta)$ and Q_0 for complex atoms

There are two methods available for the determination of the field $V(r)$ for other atoms than H and He: the self-consistent field method of Hartree,† and the statistical method due to Thomas‡ and Fermi§ in which the atomic electrons are treated as a degenerate gas. Of these two the most accurate is certainly Hartree's method. The application of this method to complicated atoms such as mercury is, however, a lengthy procedure. For the more complex atoms the method of Thomas and Fermi may be applied immediately, and since it is a statistical method it will be more accurate for such atoms than for the lighter ones.

Using potentials given by Hartree's method, the differential cross-sections for collisions of electrons with various atoms may be calculated by numerical integration from the formula (4). Actually the self-consistent field was first used for the calculation of the F -factors|| involved in the scattering of X-rays by crystals, and the corresponding values for the scattering of electrons may be obtained from these by means of the relation

$$I(\theta) = \frac{e^4}{4m^2v^4} (Z - F)^2 \operatorname{cosec}^4 \frac{1}{2}\theta \quad (11)$$

obtained in Chap. VII, eq. (8). In Table II the values of $I(\theta)$ calculated in this way are given for a number of atoms as a function of $V^{\frac{1}{2}} \sin \frac{1}{2}\theta$, where V is the electron energy in volts and θ is the angle of scattering. For all atoms the resulting angular distribution falls off uniformly with

† *Proc. Camb. Phil. Soc.* **24** (1927), 89, 111, and 426.

‡ *Ibid.* **23** (1926), 542.

§ *Zeits. f. Physik*, **48** (1928), 73.

|| Cf. James and Brindley, *Zeits. f. Crystall.* **78** (1931), 470.

TABLE II
I(θ) calculated from Hartree Fields

To obtain cross-sections in absolute units multiply by 5.66×10^{-20} .

$\frac{\sin \frac{1}{2}\theta}{\lambda} \times 10^{-8}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1
$\sqrt{(\text{Volts})\sin \frac{1}{2}\theta}$	1.22	2.45	3.67	4.90	6.12	7.35	8.57	9.80	11.02	12.25	13.47
Li	6400	900	275	112	64	36	24	15	10	7	5
Be	12100	2760	655	225	108	61	37	23	17	12	8
B	22500	4220	1180	425	196	100	59	35	24	17	13
C	19600	5610	1780	655	295	148	88	53	35	25	18
N	14400	4900	1960	860	415	222	123	74	48	32	23
O	8100	4550	2080	1020	540	295	172	104	67	45	31
F	14400	4900	2560	1240	645	361	210	130	85	56	40
Ne	4900	3900	2180	1220	700	420	256	156	106	72	49
Na	18200	4900	2280	1290	772	470	289	188	126	85	59
Mg	22500	7200	2820	1890	830	515	327	220	149	100	70
Al	40000	10200	3400	1600	900	558	361	237	164	114	83
Si	70000	13200	4150	1830	1000	610	400	275	188	130	94
P	67600	15600	5300	2220	1160	675	436	289	204	144	104
S	57600	17400	6130	2600	1340	770	480	324	222	160	116
Cl	57600	20300	7410	3130	1520	850	530	346	243	173	125
A	48400	18200	7100	3380	1660	930	580	380	268	193	142

increase in angle of scattering. At a given velocity of impact the rate of decrease of scattering with angle is greater, the smaller the atomic number of the element concerned.

4.1. Use of the Thomas-Fermi field. High-velocity encounters†

In the method of Thomas and Fermi we introduce the auxiliary variables ϕ , x , defined by

$$Z\epsilon\phi = rV(r)$$

$$x = 2^{13/3}3^{-2/3}\pi^{4/3}m\epsilon^2\hbar^{-2}Z^{1/3}r. \quad (12)$$

Then ϕ satisfies the differential equation

$$\frac{d^2\phi}{dx^2} = \phi^{3/2}x^{-1/2},$$

subject to the boundary conditions

$$\phi(0) = 0, \quad \phi(\infty) = 0.$$

The quantity x/r defines the reciprocal of an 'atomic radius' which we see is a monotonic function of Z .

The function ϕ has been tabulated by Fermi as a function of x , and

† Bullard and Massey, *Proc. Camb. Phil. Soc.* **26** (1930), 556.

so $V(r)$ may readily be obtained from this table and the equations (12). On substitution in the expression for $I(\theta)$ we obtain

$$I(\theta) = \left[\frac{3^{4/3} h^2 Z^{1/3}}{2^{17/3} \pi^{2/3} \epsilon^2 m \mu} \int_0^\infty \phi(x) \sin \mu x \, dx \right]^2, \quad (13)$$

where

$$\mu = 3^{2/3} h v \sin \frac{1}{2} \theta / (2^{7/3} \pi^{1/3} \epsilon^2 Z^{1/3}).$$

Since $\phi(x)$ is independent of Z , we see that $I(\theta)Z^{-2/3}$ is a function of μ only, i.e. of $Z^{-1/3}v \sin \frac{1}{2}\theta$ only. As a consequence $I(\theta)$ may be obtained for all atoms, if a table is prepared giving $I(\theta)Z^{-2/3}$ as a function of $Z^{-1/3}v \sin \frac{1}{2}\theta$. In general this can only be done by numerical integration; but in the special case of large μ , corresponding to high velocities of impact, an approximate explicit expression for $I(\theta)$ may be obtained. This is†

$$I(\theta) \sim \frac{Z^2 \epsilon^4 \operatorname{cosec}^4 \frac{1}{2} \theta}{4m^2 v^4} \left\{ 1 - 6.4 \times 10^{-4} \left(\frac{\operatorname{cosec} \frac{1}{2} \theta}{\beta} \right)^{3/2} Z^{1/2} \right\},$$

where $\beta = v/c$.

This formula shows that for these fast collisions the Rutherford formula is a close approximation. The second term, which represents the effect of the atomic electrons, does not resemble in any way the correction, often applied, of substituting $Z^2 + Z$ for Z^2 in the Rutherford formula, but it must be remembered that no inelastic collisions have been taken into account in deriving the result. As an example of the magnitude of the correction, we find that for the scattering of 70-kilovolt electrons by gold atoms the correction‡ to the Rutherford formula is 25 per cent. for angles of scattering of 20° .

The numerical integration required to tabulate $I(\theta)Z^{-2/3}$ as a function of μ (i.e. of $Z^{-1/3}v \sin \frac{1}{2}\theta$) was first begun by Mitchell§ for a few values of μ and completed over the whole range from $\mu = 0$ to $\mu = 15$ by Bullard and Massey.|| The results of these calculations are embodied in Table III.

Comparison with the values given by the Hartree field shows that the two methods give equivalent results for the heavier atoms, but disagree for the lighter, particularly for those atoms with abnormal sizes such as the rare gases and the alkali metals. The statistical method naturally takes no account of individual differences between atoms and so does not apply satisfactorily to these atoms.

† Bullard and Massey, *Proc. Camb. Phil. Soc.* **26** (1930), 556.

‡ This correction takes no account of any relativistic effects.

§ *Proc. Nat. Acad. Sci.* **15** (1929), 520.

|| *Proc. Camb. Phil. Soc.* **26** (1930), 556.

TABLE III

Scattered Intensities calculated from the Thomas-Fermi Field

μ	$\frac{\sqrt{(\text{Volts})\sin \frac{1}{2}\theta}}{Z^{1/3}}$	$I(\theta)/Z^{2/3}$ $\times 10^{-18} \text{ cm.}^2$
0	0	2160
0.03	0.062	2120
0.05	0.104	2010
0.1	0.208	1460
0.2	0.41	678
0.3	0.62	344
0.4	0.83	202
0.5	1.04	122
0.6	1.25	79
0.7	1.46	54
0.8	1.66	44.0
0.9	1.87	29.6
1.0	2.08	18.7
1.5	3.12	6.43
2.0	4.16	2.52
3.0	6.25	0.61
5.0	10.4	0.089
6.0	12.5	0.046
7.0	14.6	0.026
8.0	16.7	0.016
9.0	18.7	0.010
10.0	20.8	0.0064
12.0	25.0	0.0032
15.0	31.2	0.0013

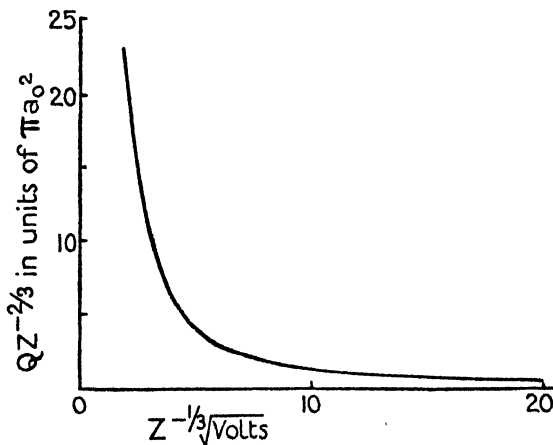


FIG. 23. Total elastic cross-sections calculated by use of the Thomas-Fermi field.

The calculation of total cross-sections may be carried out by a second numerical integration. It may easily be seen that $QZ^{-2/3}$ is a function of $vZ^{-1/3}$ only. This function is illustrated in Fig. 23; it is important to note that the cross-section is a monotonic function of the velocity.

5. The validity of Born's first approximation

The exact formula (Chap. II, eq. (17)) for the differential cross-section is

$$I(\theta) d\omega = \frac{1}{4k^2} \left| \sum_{n=0}^{\infty} (2n+1)(e^{2i\eta_n} - 1)P_n(\cos \theta) \right|^2 d\omega. \quad (14)$$

In Chap. VII, § 2, it was shown that the Born formula can be expanded in the form

$$I(\theta) d\omega = \frac{1}{k^2} \left| \sum_{n=0}^{\infty} (2n+1)\zeta_n P_n(\cos \theta) \right|^2 d\omega, \quad (15)$$

where

$$\zeta_n = -\frac{4\pi^3 m}{\hbar^2} \int_0^{\infty} V(r)[J_{n+\frac{1}{2}}(kr)]^2 r dr. \quad (16)$$

The two formulae will thus give identical results if $\exp(2i\eta_n) - 1$ may be replaced by $2i\zeta_n$. This can clearly only be the case if ζ_n is small, and in Chap. II, § 2, it was shown that under these conditions ζ_n is a good approximation to η_n . We have then, as the condition of accuracy of Born's formula, for all angles θ , that

$$\frac{4\pi^3 m}{\hbar^2} \int_0^{\infty} V(r)[J_{n+\frac{1}{2}}(kr)]^2 r dr \ll 1, \quad \text{for all } n. \quad (17)$$

When this condition is satisfied for most, if not all, values of n which contribute significantly to the sum (14), then we can expect that, for small angles, Born's approximation will still remain valid. This has already been discussed in Chap. VII, § 5, in which it was shown that the condition

$$V(1/k\theta) \ll E\theta \quad (18)$$

must be satisfied in order that Born's approximation should be valid for scattering through an angle θ , E being the kinetic energy of the incident particles.

Table IV gives a comparison, for hydrogen and helium, of the exact values η_n of the phases for a number of electron energies, † with approximate values ζ_n calculated from (16) by means of the formula

$$\zeta_n = \frac{4\pi^2 m \epsilon^2}{k\hbar^2} \left(1 - \frac{1}{2} Z \frac{\partial}{\partial Z} \right) Q_n \left(\frac{2Z^2 + k^2 a_0^2}{k^2 a_0^2} \right), \quad (19)$$

† Calculated by Macdougall, *Proc. Roy. Soc. A*, **136** (1932), 549, by numerical integration of the appropriate differential equations.

where Q_n is a spherical harmonic of the second kind. This gives in particular

$$\zeta_0 = \frac{2\pi^2 m \epsilon^2}{k \hbar^2} \left\{ \log \left(1 + \frac{k^2 a_0^2}{Z^2} \right) + \frac{k^2 a_0^2}{Z^2 + k^2 a_0^2} \right\}.$$

An estimate is also given of the number of phases required when the exact expression (14) for the scattering is used.†

TABLE IV
Comparison of Exact and Approximate Expressions for Phases

<i>Helium</i>		η_0		η_1		η_2		<i>Number of terms required</i>
ka_0	<i>Volts</i>	<i>Exact</i>	<i>Born</i>	<i>Exact</i>	<i>Born</i>	<i>Exact</i>	<i>Born</i>	
1.05	15	1.360	0.565	0.052	0.042	0.0065	0.0054	1
1.92	50	1.093	0.734	0.186	0.148	0.0411	0.0329	4
3.00	122	0.898	0.731	0.272	0.224	0.0946	0.0769	6
4.00	215	0.784	0.687	0.301	0.264	0.1304	0.1130	8
5.00	340	0.696	0.638	0.308	0.274	0.1524	0.1378	10

<i>Hydrogen</i>		η_0		<i>Number of terms required</i>
ka_0	<i>Volts</i>	<i>Exact</i>	<i>Born</i>	
1.0	13.5	0.905	0.596	1
2.0	54	0.694	0.602	3
3.0	122	0.568	0.534	5
4.0	215	0.490	0.472	6
5.0	340	0.432	0.422	8

It would appear from a study of this table that the approximation should be fairly accurate for electrons with energy > 100 e.V. in helium and > 75 e.V. in hydrogen. This is in agreement with the available experimental evidence discussed in § 3.1 of this chapter.

Table V gives some values of ζ_0 calculated numerically from (16) using the Fermi-Thomas fields of the heavier rare gases, together with the approximate number of terms required in the expansion (14).

TABLE V

	<i>Voltage</i>	ζ_0	n	<i>Voltage</i>	ζ_0	n
Neon	20	4.5	2	2,000	2.0	10
Argon	30	5.6	4	3,000	2.9	20
Krypton	48	8.8	5	4,800	4.65	30
Xenon	64	11.5	6	6,400	6.1	40

n = approximate number of terms required in series of partial cross-sections.

From these figures we expect that Born's formula should be fairly

† For these light atoms the criterion (18) is not precise enough to be of much assistance in determining the angular range of validity for any given electron energy.

accurate at about 1,000 e.V. in neon and argon and possibly also in krypton, whereas xenon is more doubtful.

At sufficiently high electron energies the Born formula will be completely valid—all the phases being small. As the energy is reduced the phases increase. In general, at a fixed energy, they decrease with n , so the first phase to become too large, to be given accurately by (16), will be η_0 . Under these conditions we may write

$$I(\theta) = \left| \{I_b(\theta)\}^\dagger + \frac{1}{2ik}(e^{2i\eta_0} - 1 - 2i\zeta_0) \right|^2, \quad (20)$$

where I_b is the scattered intensity given by the Born formula. The deviation of the scattering from Born's approximation will be most marked where $I_b(\theta)$ is small, i.e. at large angles. As the correcting term does not vary with the angle, the scattering should first deviate by remaining nearly constant at large angles instead of falling off uniformly. Referring to Fig. 22 we see that this is just the way in which the observed curves for helium do deviate at large angles. The progressive increase in importance of the deviation as the electron energy decreases from 700 to 100 e.V. is also manifest.

If the atom is heavy enough, contributions due to departure of $\exp(2i\eta_1) - 1$, $\exp(2i\eta_2) - 1$, etc., from $2i\zeta_1$, $2i\zeta_2$, etc., will become important as the electron energy decreases. When this is the case the departures from Born's approximation at large angles will vary with angle in a more complicated fashion. Fig. 24 illustrates experimental results obtained by Arnot† for the scattering of electrons by the heavier rare gases. At the electron energies indicated Born's formula gives good results for neon over the complete angular range investigated (15–120°), and for argon, krypton, and xenon up to angles of 80°. For greater angles of scattering small deviations may be observed for these heavy gases (see Fig. 24(b)). The nature of these deviations indicates that, whereas for argon they arise from the zero-order term only, higher-order terms are also affected for krypton and xenon. As the energy of the incident electrons is decreased the angular range of validity of Born's formula is found to decrease, as expected. Thus, for 200 e.V. electrons in neon, the formula fails at angles beyond 90°. The agreement between theory and experiment is thus very satisfactory.

6. Multiple scattering

So far we have considered the distribution in angle of electrons which have suffered single scattering only. In many experimental conditions,

† *Proc. Roy. Soc. A*, **133** (1931), 615.

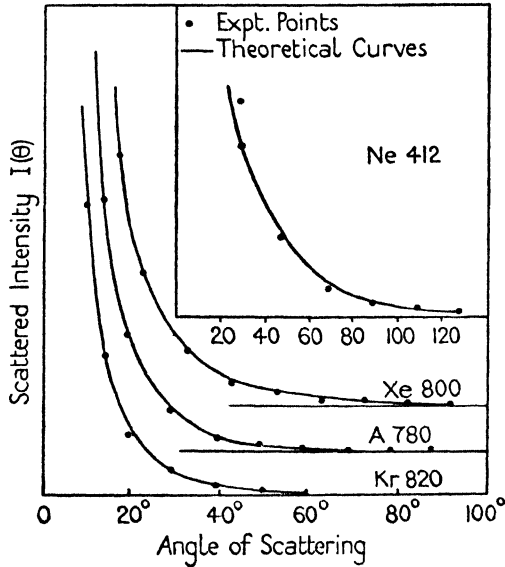


FIG. 24(a). Small angle scattering.

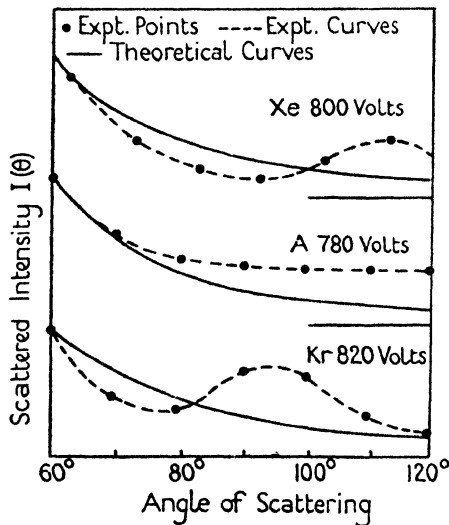


FIG. 24(b). Large angle scattering.

Angular distributions of electrons scattered by rare gas atoms.

however, the distribution observed is a mean resulting from multiple scattering of the electrons. Thus it is usually much more convenient to observe multiple rather than single scattering through small angles.

Furthermore, the effect of multiple scattering in producing spurious curvature of tracks in a cloud chamber may often be so serious as to mask completely the effect due to an applied external magnetic field. It is therefore important to consider the multiple scattering in some detail.

The essential features have been brought out very clearly in a simple treatment due to E. J. Williams.† We consider a beam of electrons of velocity v incident on a foil of thickness t containing N atoms/c.c. of atomic number Z . Then the chance that an electron will suffer a single deviation through an angle between θ and $\theta + d\theta$ is given by

$$P(\theta) d\theta = 2\pi NtI(\theta)\sin\theta d\theta, \\ \simeq \{8\pi NtZ^2\epsilon^4/(m^2v^4\gamma^2)\} d\theta/\theta^3, \quad (21)$$

where

$$\gamma^2 = (1 - v^2/c^2)^{-1},$$

provided the angle of scattering is small, the shielding effect of the atomic electrons is negligible, and $Z\epsilon^2/\hbar c$ is $\ll 1$ (see Chap. IV (42)). We now define an angle θ_1 , such that the chance of a deviation through an angle $> \theta_1$, is unity. Thus

$$\theta_1^2 \simeq \kappa, \quad (22)$$

where

$$\kappa = 4\pi NtZ^2\epsilon^4/(m^2v^4\gamma^2). \quad (23)$$

Owing to the rapid increase of scattering probability with decreasing angle there will be a great number of collisions in which the deviations are appreciably less than θ_1 . These will give rise to an approximately Gaussian distribution for the resultant deflexion, viz.

$$P_1(\alpha) d\alpha = \frac{2}{\pi\bar{\alpha}} \exp\left\{-\frac{1}{2} \frac{\alpha^2}{\bar{\alpha}^2}\right\} d\alpha, \quad (24)$$

where $\bar{\alpha}$ is the arithmetic mean, and $\bar{\alpha}^2$ the mean square, of α . Hence $\bar{\alpha}^2$ is the sum of the squares of individual deflexions which build up to α , giving

$$\bar{\alpha}^2 = \int_0^{\theta_1} \theta^2 P(\theta) d\theta \\ = 2\kappa [\log \theta]_0^{\theta_1}, \quad (25)$$

according to (21) and (22).

To obtain a finite result we must allow for the shielding by the atomic electrons. This reduces the scattering through angles $< \theta_{\min}$ to a negligible value. The value of θ_{\min} depends on whether the Born or classical

† *Proc. Roy. Soc. A*, **169** (1938), 531; *Phys. Rev.* **58** (1940), 292; *Rev. Mod. Phys.* **17** (1945), 217.

approximation is valid, i.e. according as $Z\epsilon^2/\hbar v$ is \ll or $\gg 1$, respectively. If a is the effective distance from the nucleus at which shielding becomes important then, as shown in Chap. VII, § 5,

$$\theta_{\min} \simeq h/(2\pi m v \gamma a) \quad (Z\epsilon^2/\hbar v \ll 1), \quad (26)$$

$$\simeq Z\epsilon^2/(m v^2 \gamma a) \quad (Z\epsilon^2/\hbar v \gg 1). \quad (27)$$

In applications to electrons (26) is usually the appropriate approximation, giving

$$\bar{\alpha}^2 = 2\theta_1^2 \log\{2\pi m v \gamma a \theta_1/h\}. \quad (28)$$

The scattering remains multiple for angles $< \theta_2$ where

$$P_1(\theta_2) = P(\theta_2).$$

In order that the approximation be valid so that the average deflexion be due almost entirely to multiple scattering we must have

$$\theta_2 > \bar{\alpha} > \theta_1.$$

This requires that

$$\theta_1 \gg \theta_{\min},$$

or, substituting from (26) and (22),

$$16\pi^3 N t Z^2 \epsilon^4 a^2 / (h^2 v^2) \gg 1. \quad (29)$$

On the basis of the Fermi-Thomas statistical model of the atom, a is of order $Z^{-1/3} a_0$, so the condition becomes

$$N t Z^{4/3} / \beta^2 \gg \pi m^2 c^2 / h^2$$

where $\beta = v/c$.

$$= 0.52 \times 10^{20},$$

To obtain a more definite value for the shielding distance we note that, on the assumption of the Fermi-Thomas atomic field, $I(\theta)Z^{-2/3}$ is a function of $Z^{-1/3} m v \gamma \sin \frac{1}{2}\theta/\hbar$ given in Table III. For small angles θ we may write

$$I(\theta) = \{4Z^2 \epsilon^4 / (m^2 v^4 \gamma^2 \theta^4)\} g(Z^{-1/3} m v \gamma a_0 \theta/\hbar). \quad (30)$$

θ_{\min} is defined by

$$\int_0^{\theta_1} g(Z^{-1/3} m v \gamma a_0 \theta/\hbar) d(\log \theta) = \log(\theta_1/\theta_{\min}). \quad (31)$$

Numerical integration then gives

$$\theta_{\min} = 2.10 Z^{1/3} \hbar / (m v \gamma a_0), \quad (32)$$

$$= 0.0153 Z^{1/3} / (\beta \gamma),$$

so that (28) becomes

$$\bar{\alpha}_1^2 = 2\theta_1^2 \log(65.3 \beta \gamma Z^{-1/3} \theta_1). \quad (33)$$

If $I(\theta)$ is calculated using the Hartree field (Table II), the numerical

value of the coefficient is changed from 2.10 by a small amount. However, as it only appears logarithmically, there is no serious error introduced by using the Fermi-Thomas value for all but the lightest atoms.

Williams has also calculated the appropriate expression for θ_{\min} when classical scattering prevails. He finds, again using the Fermi-Thomas field, that

$$\theta_{\min} = 3.8Z^{4/3}\epsilon^2/(mv^2\gamma a_0). \quad (34)$$

An important application of multiple-scattering theory is to the tracks of fast particles in a cloud chamber. Here it is not the angle θ which is observed, but its projection ϕ on the plane perpendicular to the line of sight. Following an exactly similar method, the mean square average angle $\bar{\delta}^2$ of projected scattering is found to be

$$\bar{\delta}^2 = \{4\pi N x Z^2 \epsilon^4 / (m^2 v^4 \gamma^2)\} \log(\phi_{\max}/\phi_{\min}), \quad (35)$$

where

$$\begin{aligned} \phi_{\min} &= 1.75Z^{1/3}\hbar/(mv\gamma a_0) \\ &= 0.0128Z^{1/3}/(\beta\gamma). \end{aligned}$$

x is the path length of the track and ϕ_{\max} may be taken as the maximum angle easily recognized as single scattering (about 0.1 radian). This gives rise to a spurious radius of curvature ρ_s of the track, where†

$$\rho_s = \left(\frac{3}{2}\right)^{\frac{1}{2}} \frac{x}{\bar{\delta}^2}. \quad (36)$$

A more rigorous theory of multiple scattering has been given by Goudsmit and Saunderson‡ which confirms the accuracy of the simpler theory to within a few per cent.

Let $p(\theta)d\omega$ be the chance that, in a collision, the particle will be scattered into the solid angle $d\omega$, i.e.

$$p(\theta) = I(\theta)/Q,$$

where Q is the total cross-section. Consider $p(\theta)$ to be expanded in the form

$$p(\theta) = \sum (2n+1)f_n P_n(\cos\theta). \quad (37)$$

Then, after two collisions, the chance of finding the particle moving in the solid angle $d\omega$ about θ, ϕ will be given by

$$p_2(\theta)d\theta = \int_0^\pi \int_0^{2\pi} \frac{p(\theta_1)}{2\pi} \frac{p(\theta_2)}{2\pi} \sin\theta_1 \sin\theta \, d\theta_1 d\phi_1 d\theta d\phi, \quad (38)$$

where $\cos\theta_2 = \cos\theta \cos\theta_1 + \sin\theta \sin\theta_1 \cos(\phi_1 - \phi)$.

Using the formula

$$P_n(\cos\theta_2) = P_n(\cos\theta)P_n(\cos\theta_1) + \sum \frac{(n-m)!}{(n+m)!} P_n^m(\cos\theta)P_n^m(\cos\theta_1)\cos m(\phi - \phi_1),$$

we find

$$p_2(\theta) = \sum (2n+1)(f_n)^2 P_n(\cos\theta), \quad (39)$$

and, in general, after s collisions

$$p_s(\theta) = \sum (2n+1)(f_n)^s P_n(\cos\theta). \quad (40)$$

† Bethe, *Phys. Rev.* **70** (1946), 821.

‡ *Phys. Rev.* **57** (1940), 24, and **58** (1940), 39.

If $W(s)$ is the chance that a particle suffers s collisions, the multiple-scattering angular distribution function is given by

$$p_m(\theta) = \sum W_s p_s(\theta).$$

Taking for W_s the Poisson distribution

$$W_s = e^{-\nu} \nu^s / s!, \quad (41)$$

where ν is the chance of one collision,

$$p_m(\theta) = \sum (2n+1) \exp\{-\nu(1-f_n)\} P_n(\cos \theta). \quad (42)$$

For scattering by the Fermi-Thomas field, Goudsmit and Saunderson obtain

$$\exp\{-\nu(1-f_n)\} = \exp\left[\frac{1}{2}n(n+1)\kappa\left\{\log\left(\frac{1}{2}\theta_{\min}\right) - \sum_2^n s^{-1}\right\}\right], \quad (43)$$

where θ_{\min} is as given by (32). Using the formulae (42) and (43) it may be shown that, to a high degree of approximation, the multiple-scattering distribution is Gaussian with

$$\bar{\alpha}_1^2 = 2\kappa \log(0.64\theta_1/\theta_{\min}). \quad (44)$$

This is to be compared with Williams's result

$$\bar{\alpha}_1^2 = 2\kappa \log(\theta_1/\theta_{\min}).$$

The most complete series of experiments on multiple scattering of fast electrons have been carried out by Kulchitsky and Latyshev.† They used homogeneous electron beams of 2.25 M.e.V. energy scattered by foils, the scattered current being measured by counters. The comparison of their experimental results with the theories of Williams and of Goudsmit and Saunderson is shown in Table VI. It will be seen that

TABLE VI

Comparison of Observed and Calculated Half-Widths of Multiple Scattering Distribution for 2.25 M.e.V electrons

Element	M	$Zc^2/h\nu$	Half-width of Gaussian distribution (degrees)			
			Obs.	Williams's theory		Goudsmit and Saunderson theory Born
				Classical	Born	
Al	60.2	0.10	9.50	12.1	9.8	9.4
Fe	41.4	0.20	9.60	11.9	9.9	9.6
Cu	46.8	0.22	10.40	10.4	11.05	10.5
Mo	36.6	0.32	10.25	..	10.75	10.35
Ag	35.1	0.36	10.20	..	10.80	10.30
S	34.2	0.37	10.65	11.9	10.90	10.65
Ta	28.7	0.55	9.85	..	11.00	10.95
Au	29.4	0.60	9.9	..	11.40	11.35
Pb	26.1	0.62	9.7	10.6	10.85	10.85

$M = \frac{2\hbar^2}{m^2 c^2} \frac{NtZ^{4/3}}{\beta^2}$, which must be $\gg 1$ in order that Williams's theory be applicable (see (20)).

† *Phys. Rev.* 61 (1942), 260.

the two theories give nearly the same results. For all but the three heaviest elements the agreement with experiment is very good, especially with the more rigorous theory, provided the Born and not the classical expression for the angle θ_1 of cut-off is used. This would be expected for, in all these cases, $Ze^2/\hbar v$ is considerably less than unity.† For the heaviest elements investigated, the theoretical distributions, which agree closely, give half-widths between 10 and 15 per cent. too large. Exact agreement would not be expected as, for these elements, relativistic effects are no longer given to a close approximation by the expression (21).

These general conclusions are confirmed from the work of other investigators. In earlier work,‡ in which cloud chambers were used, the discrepancies with theory were somewhat greater; but in the most recent cloud-chamber observations of Oleson, Chao, and Crane§ they are reduced to much the same value as in the work of Kulchitsky and Latyshev.

† Contrast this with the multiple scattering of α -particles (Chap. XII, § 2.4) for which $Ze^2/\hbar v$ and the classical approximation gives the best results.

‡ Oleson, Chao, Halpern, and Crane, *Phys. Rev.* **56** (1939), 482 and 1171; Sheppard and Fowler, *ibid.* **57** (1940), 273; Crane and Slawsky (quoted by Goudsmit and Saunderson, *ibid.* **58** (1940) 39).

§ *Ibid.* **60** (1941), 378.

ELASTIC SCATTERING OF SLOW ELECTRONS BY ATOMS

1. The Ramsauer and Townsend effects

As was shown in Chap. IX, § 5, Born's first approximation is not applicable to low-velocity collisions of electrons with atoms, and the experimental results obtained in this region show clearly that a more elaborate theory is required.

In a preliminary investigation in 1921 of the free paths of electrons of very low velocity (0.75 to 1.1 volts) in various gases, Ramsauer† found the free paths of these electrons in argon to be very much greater than that calculated from gas-kinetic theory. The extension of these observations to a wider range of velocities‡ revealed a surprising variation in the cross-section. It was found that the effective cross-section (proportional to the reciprocal of the free path) of argon atoms increases with decreasing velocity until the electron energy becomes less than 10 volts. For electron energies below this value it decreases again to the low values found in the preliminary measurements. Independently, Townsend and Bailey§ examined the variation of free path with velocity for electrons with energies between 0.2 and 0.8 volts by a different method, and showed that a maximum of the free path occurs at about 0.39 volts. This was confirmed by much later work of Ramsauer and Kollath.||

Since these classical experiments were carried out, the behaviour of a large number of gases and vapours has been examined over a wide voltage range.†† The results obtained are illustrated in Fig. 25 for some monatomic gases and vapours. In these figures the variation of effective cross-section with velocity is illustrated. This is proportional to the reciprocal of the mean free path. For purposes of comparison the gas-kinetic cross-section is indicated on the figures.

The striking features of the cross-section-velocity curves are their wide variation in shape and size and also the marked similarity of behaviour of similar atoms, such as those of the heavier rare gases and the alkali metal vapours. At the time of the earlier measurements no satisfactory explanation of the phenomena could be given, but on the

† *Ann. der Phys.* **64** (1921), 513.

‡ Ramsauer, *ibid.* **66** (1921), 545.

§ *Phil. Mag.* **43** (1922), 593; **44** (1922), 1033.

|| *Ann. der Phys.* **3** (1929), 536.

†† See, for example, the summaries by Kollath, *Phys. Zeits.* **31** (1931), 985; Brode, *Rev. Mod. Phys.* **5** (1933), 258; McMillen, *ibid.* **11** (1939), 84; Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chap. I.

introduction of quantum mechanics it was immediately suggested that the effect was a diffraction phenomenon. Thus Bohr† suggested in general terms how the minimum cross-section observed in the rare gases near 0.7 volts could be explained. The field of a rare gas atom falls off

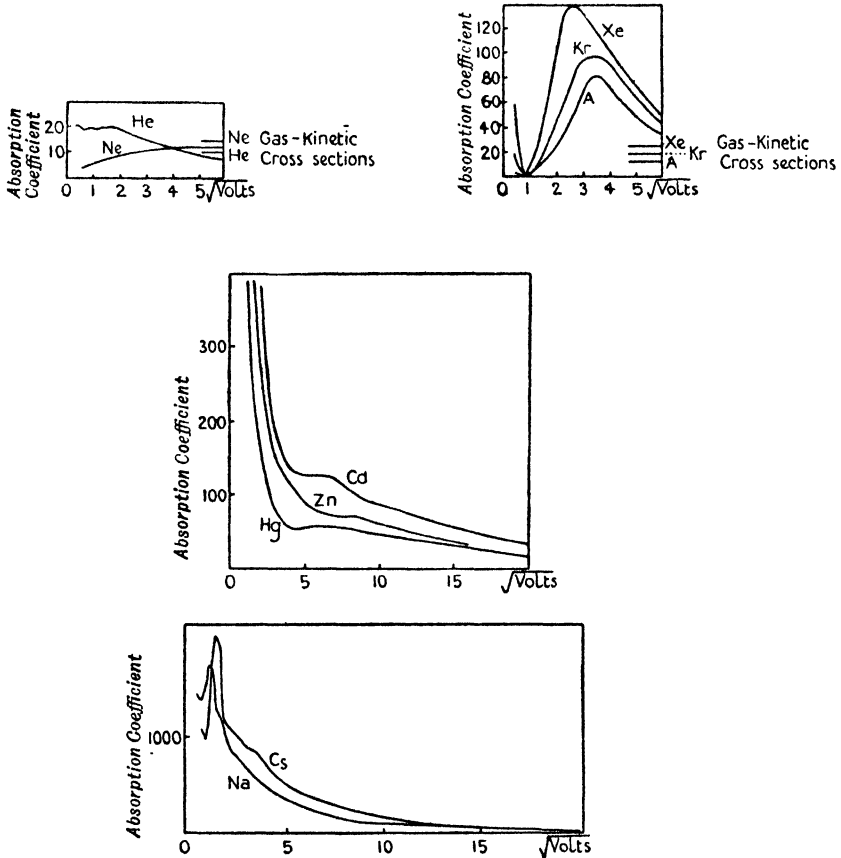


FIG. 25. Observed variation of effective cross-sections with electron velocity.

very much more rapidly with distance than that of any other atom, and might be expected to behave in much the same way as a spherical potential well, discussed in Chap. II, § 3. It was shown there that the well may be deep enough to introduce within its range one or more complete wave-lengths of zero angular momentum without affecting waves of higher angular momentum appreciably. An observer at a great distance from the atom will then fail to observe any scattering.

Strong experimental evidence of the wave nature of the phenomena

† In conversation with Professor R. H. Fowler.

was afforded by measurements of the angular distributions of the elastically scattered electrons. These were first carried out for electrons of energy between 4 and 40 volts by Bullard and Massey for argon.†

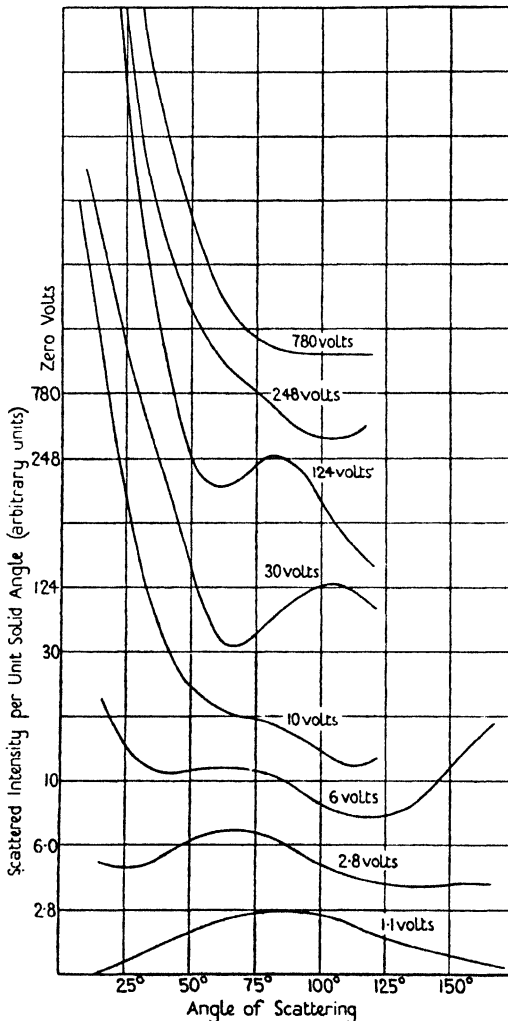


FIG. 26. Observed angular distributions of electrons scattered elastically by argon atoms.

Instead of the curves characteristic of Born's first approximation, showing a monotonic decrease of intensity with angle of scattering, the curves obtained by Bullard and Massey exhibit maxima and minima. In Fig. 26 a series of curves is given illustrating the variation in form of

† *Proc. Roy. Soc. A*, 130 (1931), 579.

these curves, for argon, as the electron velocity increases from 1.1 volts to 780 volts; they show the gradual transition to the curves predicted by Born's first approximation. The higher voltage measurements (42–780 volts) are due to Arnot,[†] and at the lowest voltages (1.1 and 2.8 volts) to Ramsauer and Kollath.[‡] These experiments have now been carried out for a large number of gases over a wide range of electron energies, and it is found that in the majority of cases maxima and minima occur in some voltage range.[§] For light gases, such as hydrogen

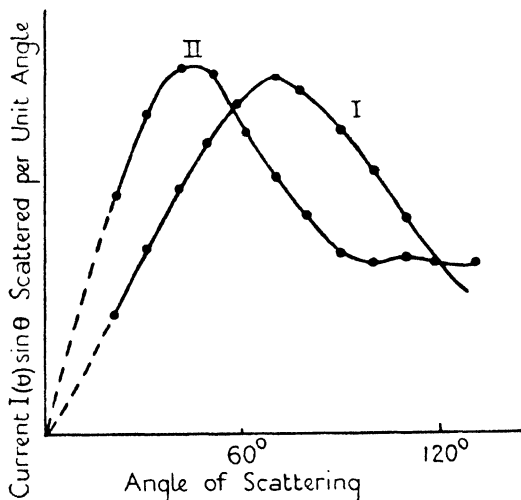


FIG. 27. Illustrating the finite scattering through small angles. I. Curve for 6 volt electrons scattered by neon atoms. II. Curve for 7 volt electrons scattered by nitrogen molecules.

and helium, this range is small (up to 15 volts in helium and 6 volts in hydrogen), while for mercury pronounced maxima and minima are observed up to the highest voltages for which observations have been taken (800 volts). From these experiments it is obvious that the wave nature of the electron is important over a wider range than is apparent from the observation of effective cross-sections.

It is of interest to examine the evidence from the angular distribution measurements as to the validity of the theoretical result (Chap. VII, § 1.1) that the function $2\pi I(\theta)\sin\theta$, giving the number of electrons scattered per unit angle by a gas atom, tends to zero as θ tends to zero. In Fig. 27 two experimental curves representing scattering per unit angle

[†] *Ibid.* A, 133 (1931), 615.

[‡] *Ann. der Physik*, 12 (1932), 529.

[§] See McMillen, *Rev. Mod. Phys.* 11 (1939), 84, and Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chap. II.

are illustrated, and it is seen that the evidence is in favour of the theoretical conclusion.

2. The theory of the scattering of low-velocity electrons. Method of partial cross-sections

In order to develop a theory of the scattering of low-velocity electrons by atoms, we must refer to the general theory of Chapter VIII. The wave function Ψ , which in this case represents the system of atom + incident electron, was expanded in the form

$$\Psi = \left(\sum + \int \right) \psi_n(\mathbf{r}_a) F_n(\mathbf{r}),$$

where $\psi_n(\mathbf{r}_a)$ is the wave function representing the n th excited state of the atomic system. It was then shown that the function $F_n(\mathbf{r})$ satisfies the equation

$$(\nabla^2 + k_n^2) F_n = \frac{8\pi^2 m}{\hbar^2} \int V(\mathbf{r}, \mathbf{r}_a) \Psi(\mathbf{r}_a, \mathbf{r}) \psi_n^*(\mathbf{r}_a) d\tau_a,$$

where $V(\mathbf{r}, \mathbf{r}_a)$ is the interaction energy between the incident and atomic electrons, and k_n is the wave number of the outgoing electron wave, equal to $2\pi m v_n / \hbar$.

If we neglect electron exchange, the elastic scattering is completely determined by the function F_0 , which satisfies the equation

$$(\nabla^2 + k^2) F_0(\mathbf{r}) = \frac{8\pi^2 m}{\hbar^2} \int V(\mathbf{r}, \mathbf{r}_a) \Psi(\mathbf{r}_a, \mathbf{r}) \psi_0^*(\mathbf{r}_a) d\tau_a. \quad (1)$$

To solve (1) we must substitute some approximate form for Ψ on the right-hand side of (1). For instance, in obtaining Born's approximation in Chapter IX we neglected all the scattered waves, and replaced Ψ by $\psi_0(\mathbf{r}_a) \exp(ikz)$. In the approximation, to the examination of which this chapter is devoted, we neglect all but the elastically scattered wave, and thus set on the right-hand side of (1)

$$\Psi = \psi_0(\mathbf{r}_a) F_0(\mathbf{r}).$$

We thus obtain
$$\left\{ \nabla^2 + k^2 - \frac{8\pi^2 m}{\hbar^2} V_{00}(r) \right\} F_0(\mathbf{r}) = 0, \quad (2)$$

where
$$V_{00}(r) = \int V(\mathbf{r}, \mathbf{r}_a) \psi_0 \psi_0^* d\tau_a.$$

This is the equation which represents the motion of the incident electron in the static field of the atom, V_{00} being just the potential of this field. We have thus, to this approximation, reduced the problem to that of calculating the scattering by the static field of the atom concerned.

The method required for this calculation is described in Chap. II, § 1. Since we shall have no further occasion to consider the inelastic scattering in this chapter, we shall drop the suffix $_0$ in F_0 and V_{00} .

If we expand the function F in the form

$$F = \sum_s F_s(r) P_s(\cos \theta),$$

and substitute in (2), the function $F_s(r)$ satisfies the equation

$$\frac{d^2}{dr^2}(rF_s) + \left[k^2 - \frac{8\pi^2 m}{\hbar^2} V(r) - \frac{s(s+1)}{r^2} \right] (rF_s) = 0. \quad (3)$$

As shown in Chapter II, the solution of this equation, which is finite at the origin, will have the asymptotic form

$$rF_s \sim A_s \sin(kr - \frac{1}{2}s\pi + \eta_s),$$

η_s being a phase constant. The amplitude $f(\theta)$ of the scattered wave was shown in Chapter II to be given by

$$f(\theta) = \frac{1}{2ik} \sum_{s=0}^{\infty} (2s+1) [\exp(2i\eta_s) - 1] P_s(\cos \theta), \quad (4)$$

and the differential cross-section for elastic scattering into the solid angle $d\omega$ is

$$I(\theta) d\omega = |f(\theta)|^2 d\omega.$$

The total elastic cross-section Q is given by

$$Q = 2\pi \int_0^\pi I(\theta) \sin \theta d\theta;$$

we thus obtain

$$Q = \sum_s Q_s,$$

where

$$Q_s = 4\pi k^{-2} (2s+1) \sin^2 \eta_s. \quad (5)$$

We refer to Q_s as the partial cross-section of order s .

Born's first approximation holds only when η_s is small, so that $\sin \eta_s$ never passes through a maximum due to η_s reaching the value $\frac{1}{2}\pi$. Thus to this approximation one expects no oscillations in Q_s as a function of the energy. This is no longer the case if η_s may become greater than $\frac{1}{2}\pi$.

The classical approximation to $I(\theta)$ is never valid for electron scattering problems, but Jeffreys's method, particularly as modified by Langer (see Chap. VII, § 6.2), may usually be employed to obtain a good approximation to a phase η_s which is not too small.

It was shown in Chap. II, § 2, that, if

$$V(r) \ll \frac{s(s+1)}{r^2} \frac{\hbar^2}{2m},$$

for r given by $kr \sim \{s(s+1)\}^{\frac{1}{2}}$,

the contribution of all phases η_n with $n > s$ can be neglected. The convergence will thus be best for light atoms and slow electrons (see Chap. IX, § 5).

3. General application of the method of partial cross-sections

3.1. Condition for existence of a Ramsauer-Townsend effect

It has already been pointed out that a vanishing cross-section near the low-velocity limit can occur if the field is strong enough to introduce one or more additional wave-lengths, i.e. one or more additional zeros of the wave function F_0 within the field. For this to be possible the field must be strong enough to introduce respectively one or more discrete energy-levels of zero angular momentum. The effect cannot occur with a repulsive field for the reasons discussed in Chap. II, § 4—the phase η_0 can only equal $s\pi$ for such a field if it eliminates s complete wave-lengths which would exist if the field were not present. This is not possible at low energies because the wave-length is then much greater than the range of the field. At higher energies it may occur, but then higher-order phases must be affected also and their contributions will prevent the total cross-section from becoming abnormally small.

Quantitative calculations, discussed in § 4, confirm this explanation of the Ramsauer-Townsend effect.

3.2. Explanation of other general features

We now give a general explanation of the following experimental facts:

1. The magnitude of the cross-section varies between wide limits, the maximum observed for the alkali metals being over 100 times that observed in neon.
2. The angular distributions of the scattered electrons show marked maxima and minima.
3. The cross-section-velocity curves have forms characteristic of the different columns of the periodic table.

In order to do this we make use of the following properties of the calculated phases:

- (a) For any atomic field η_s decreases monotonically with s .
- (b) η_s is small when, for r such that $kr \sim s + \frac{1}{2}$,

$$\frac{8\pi^2 m}{h^2} V(r) \ll \frac{s(s+1)}{r^2}.$$

It follows from (b) that the series of partial cross-sections will converge quite quickly for low-velocity impacts; the major contribution will arise from the partial cross-sections Q_s of such an order that $\eta_s \simeq \frac{1}{2}\pi$. The maximum value of the contribution from a partial cross-section of order s is

$$Q_s^{\max} = \frac{4\pi}{k^2} (2s+1).$$

We may therefore say at once that, the lower the velocity and the larger the value of s for which the phase η_s attains the value $\frac{1}{2}\pi$, the bigger will be the cross-section. Referring to the condition (b), we see that the biggest collision cross-sections will be those of atoms whose fields extend out to the greatest distances, viz. the alkali metals. If we use the empirical rules due to Slater† for the effective nuclear charges of alkali atoms, and define the diameter of an atom as the distance at which the radial charge density $r^2|\psi|^2$ of the outer shell is a maximum, the following values of the radii r_0 of various atoms are obtained:

TABLE I

	r_0 in atomic units	kr_0	
		13 volts	0.5 volt
Li	2.3	2.3	0.46
Ni	4.1	4.1	0.82
K	6.1	6.1	1.22
Zn	3.1	3.1	0.62
He	0.6	0.6	0.12
Ne	0.7	0.7	0.14
A	1.3	1.3	0.26
Kr	1.7	1.7	0.34

Note. k is measured in units of $1/a_0$.

We give also the values of kr_0 corresponding to 13 and 0.5 volt electrons. Thus, using the criterion (b), we find that for potassium at least 7 harmonics are required, and the cross-section may be greater than‡ $50\pi a_0^2$, whereas one harmonic only is required for neon, and the effective area will not be greater than $10\pi a_0^2$. For $k = 0.2/a_0$ (0.54 volt), the area may be as great as $300\pi a_0^2$ for potassium, but still not much greater than $10\pi a_0^2$ for neon or helium. There is, then, clearly no difficulty in explaining the wide range in magnitude observed in the effective cross-sections. It is equally clear that the method indicates the

† *Phys. Rev.* **36** (1930), 57.

‡ The cross-sections obtained in this way will only be approximately correct when the field is sufficiently strong to produce large phase changes. For collisions of high-velocity electrons a large number of terms are required in the series, but each is small and the total cross-section small also.

possibility of maxima and minima in the angular distribution given by (4). Again the dominant effect arises from terms in the series such that $\eta_s \simeq \frac{1}{2}\pi$. The angular distribution, then, is roughly of the form

$$I(\theta) = \text{const.} \{P_s(\cos \theta)\}^2,$$

which has s minima. This will be especially marked for the lower velocity impacts, where only a few terms of the series (4) are required and the weight factor $2s+1$ is particularly effective. Thus for electrons of 30 volts energy in argon the angular distribution is given closely by $\{P_2(\cos \theta)\}^2$. Actually the calculated phase values at this velocity are

$$\eta_0 = 2\pi + 0.885, \quad \eta_1 = 4.831, \quad \eta_2 = 1.983, \quad \eta_3 = 0.374, \quad \eta_4 = 0.159.$$

It must be realized that these remarks are only illustrative, and the actual effects produced by the sum of a number of partial cross-sections may be very complicated, particularly for heavy atoms. The diffraction of waves by spherical obstacles is a much more complicated process than diffraction by a grating or other symmetrical arrangement.

It is not possible to explain the third feature listed above in such simple terms as the preceding. The quasi-periodic behaviour of the partial cross-sections must be due to the behaviour of $\sin \eta_s$. At low velocities, for the lightest atoms, only the zero-order phase is appreciable. An atomic field will behave qualitatively in a similar way to the potential well discussed in Chap. II, § 3. At a given velocity, for some atomic field, the phase η_0 will attain a value near $\frac{1}{2}\pi$, and for some heavier atom a value of $\frac{3}{2}\pi$ will be attained, giving an equal maximum of the zero-order cross-section, and so on. For some atom with intermediate properties η_1 will become appreciable, and so on. In this way some quasi-periodic behaviour of the cross-sections might be expected, but we still require to show from the theory that the periodicity follows that of the periodic table. This was first done by Allis and Morse† using a simplified atomic model. They took for the atomic field the form

$$\begin{aligned} V &= Z\epsilon^2 \left(\frac{1}{r} - \frac{1}{r_0} \right) & (r \leq r_0), \\ &= 0 & (r \geq r_0), \end{aligned} \tag{6}$$

which makes possible an analytic solution of equation (3). In order to illustrate the periodic behaviour of the cross-sections two quantities, x and β , were defined such that

$$\beta^2 = Zr_0/2a_0, \quad x = kr_0.$$

The first of these depends only on the atomic field, while the second is

† *Zeits. f. Physik*, **70** (1931), 567.

a function also of the incident electron velocity. Allis and Morse then showed that the cross-sections are quasi-periodic in β with period unity. This is illustrated in Fig. 28, where a number of partial cross-sections corresponding to different values of x are illustrated as functions of β .† If, now, the approximate atomic radii given by Slater are used (given above in Table I) and the constant Z above is adjusted to give as good agreement as possible of the form (6) for V with that obtained from

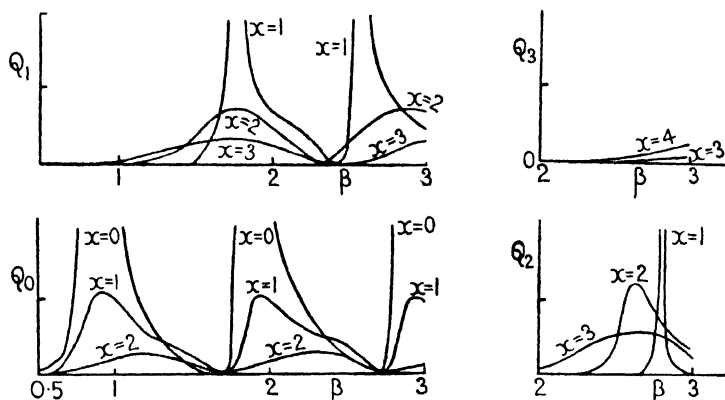


FIG. 28. Illustrating quasi-periodicity of partial cross-sections.

Slater's values, it is found that a period of 1 in β is approximately a whole period in the periodic table. This may be seen from the following values of β :

TABLE II

Lithium	1.36	Helium	0.77
Sodium	2.54	Neon	1.73
Potassium	3.51	Argon	2.68
		Krypton	3.66

The lighter elements are to some extent anomalous in this respect; this is also borne out by the observations (see Fig. 25 of this chapter).

4. Quantitative application of method of partial cross-sections

The first quantitative application of the theory was made by Holtsmark‡ for the scattering of electrons by argon; but we shall first consider the results obtained by Allis and Morse using their simplified model.

Having chosen the values of the parameter β and r_0 , using Slater's

† Compare the behaviour of Q_0 as function of β for $x = 0$ with the corresponding behaviour of Q_0 as function of k_0 for $k = 0$ in Fig. 4(a) of Chap. II.

‡ *Zeits. f. Physik*, 55 (1929), 437.

rules (*loc. cit.*), it was usually found that a good approximation to the observed cross-sections is obtained with this model. In Fig. 29 the experimental curves are compared with calculated curves. The values of β and r_0 used in obtaining the latter are slightly different from those obtained from Slater's rules (*loc. cit.*), but the differences are not great. In Table III the parameters which give the best fit with experiment are compared with Slater's values, both measured in atomic units.

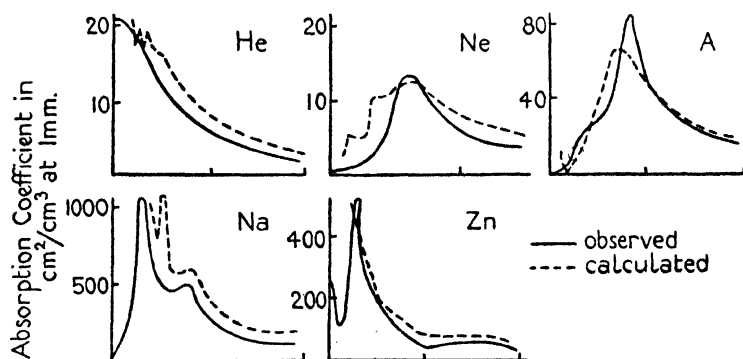


FIG. 29. Illustrating comparison of observed and calculated cross-section curves.

TABLE III

Atom	β		r_0	
	Slater	From cross-sections	Slater	From cross-sections
Helium	0.77	0.80	0.6	0.55
Neon	1.73	1.71	0.7	0.75
Argon	2.68	2.7	1.3	1.4
Sodium	2.54	2.55	4.1	4.25
Zinc	3.77	3.78	3.1	3.14

The agreement obtained is very striking and leaves little doubt as to the correctness of the theoretical explanation of the Ramsauer-Townsend effects afforded by quantum mechanics. However, the field used gives only a rough approximation, particularly for very low velocity collisions. For such cases large effects may arise from the atomic field beyond the radius r_0 . However, Morse† extended the calculations to the field

$$V = Ze^2r^{-1}\exp(-2r/r_0),$$

and found that very similar results are obtained, the same quantities β and kr_0 being again important.

Holtmark‡ obtained very good agreement with the observed cross-section for argon by using for V the Hartree field modified by an

† *Rev. Mod. Phys.* 4 (1932), 577.

‡ *Loc. cit.*

empirical polarization correction and evaluating the phases η_s by numerical integration of the differential equations. Without the polarization modification the agreement is not good.

A much stricter test of the theory may be applied by comparing calculated and observed angular distributions. These are much more sensitive to inaccuracy in the theory. In Fig. 30 the angular distribution curves observed by Bullard and Massey and by Ramsauer and Kollath

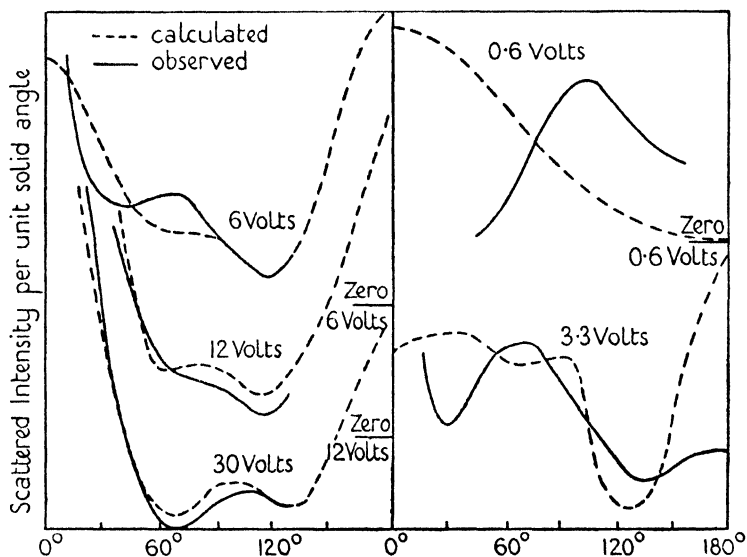


FIG. 30. Comparison of observed and calculated angular distributions of electrons scattered by argon atoms.

for argon (*loc. cit.*) are compared with those calculated by using Holtsmark's values of the phases η_s . The agreement for 30 and 12 volts is found to be extremely good in view of the peculiar nature of the experimental curves. It is of interest to note that at the lower voltages the agreement with curves calculated from the simplified model of Morse and Allis discussed in § 3 is not nearly so satisfactory. At very low velocities, however, the observations of Ramsauer and Kollath are no longer in agreement even with Holtsmark's calculations, as seen from the figure.

The exact phases have been calculated for only five other atoms, namely, for krypton by Holtsmark† using again the Hartree field modified by a polarization correction, for helium and hydrogen by Macdougall‡ using the interactions given in Chap. IX (8), for chlorine

† *Zeits. f. Physik*, 66 (1930), 49.

‡ *Proc. Roy. Soc. A*, 136 (1932), 549.

by Hartree, Kronig, and Petersen† using the unmodified Hartree field, and for oxygen by Bates and Massey‡ using the Hartree-Fock field with and without exchange and polarization corrections (see §§ 6, 7 of this chapter). For krypton the agreement with experiment is again very good, both in comparison with observed total cross-sections and with the angular distributions measured by Arnot§ and by Ramsauer and Kollath,|| except at very low voltages (less than 3 volts).

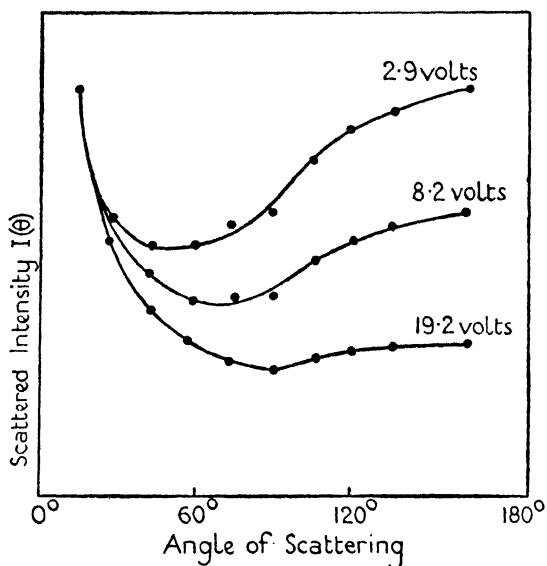


FIG. 31. Observed angular distributions of slow electrons scattered elastically by helium atoms.

In the case of helium we find the first definite indication of a failure of the theory. For such a light atom the only phase which attains a value of $\frac{1}{2}\pi$ is that of zero order, and at electron velocities below 20 volts the effect of the higher-order terms is negligible. The corresponding angular distribution is independent of angle; but the observed curves†† exhibit a minimum when the electron velocity is below 15 volts. This is illustrated in Fig. 31. The presence of this minimum at very low velocities cannot be explained by the method of partial cross-sections, and we must develop the theory further in order to provide an explanation. This is done in § 6.1. Similar behaviour is observed in molecular hydrogen. It is possible that the effect of the molecular binding is

† *Physica*, 1 (1934), 901.

‡ *Proc. Roy. Soc. A*, 192 (1947), 1.

§ *Ibid. A*, 133 (1931), 615.

|| *Ann. der Physik*, 12 (1932), 837.

†† Bullard and Massey, loc. cit.; Ramsauer and Kollath, loc. cit.

important, but it is much more likely that the reason is the same as that for helium (exchange).

For a number of other atoms calculations have been carried out in which the large phases were determined from Jeffreys's approximation (Chap. VII, § 6.2) and the small ones from Born's approximation (Chap. VII, § 6.1). To illustrate the kind of accuracy which may be attained in this way† Table IV gives the values of the phase shifts calculated for

TABLE IV

Calculated Phase Shifts for 54 Volt Electrons scattered by Krypton Atoms

Phase η_n <i>n</i>	From accurate solution	Jeffreys's approximation	Langer modification	Born approximation
0	9.696	..	9.597	..
1	7.452	7.710	7.540	..
2	4.469	4.748	4.505	..
3	1.238	1.410	1.355	0.779
4	0.445	0.557	0.535	0.414
5	0.143	0.190	0.174	0.144

54-volt electrons in krypton calculated by accurate numerical solution of the differential equation‡ and by the approximate methods.§ Values obtained by use of Langer's modification of Jeffreys's approximation are also included. It will be seen that for $\eta < 0.5$ Born's approximation is sufficiently accurate. For larger values of η Jeffreys's approximation is superior and is improved considerably for small-order phases by the Langer modification.

For mercury vapour Henneberg|| and Massey and Mohr†† carried out calculations in this way using the Thomas-Fermi field.‡‡ The calculated angular distributions are compared with Arnot's observations in Fig. 32, good general agreement being revealed. Similar calculations have been carried out for potassium,§§ zinc,|||| cadmium,|||| and bromine,††† reasonable agreement being obtained in all cases.

It appears that Faxén and Holtsmark's method gives good results for the elastic scattering of slow electrons by heavy atoms. For light atoms such as hydrogen and helium it is necessary to proceed to higher

† An empirical discussion of the effectiveness of these methods has been given by Arnot, *Proc. Camb. Phil. Soc.* **32** (1936), 161.

‡ Holtsmark, *Zeits. f. Physik*, **66** (1930), 49.

§ Arnot and Baines, *Proc. Roy. Soc. A*, **146** (1934), 651.

|| *Zeits. f. Physik*, **83** (1933), 555.

†† *Nature*, **130** (1932), 276.

‡‡ *Loc. cit.*

§§ McMillen, *Phys. Rev.* **46** (1934), 983.

|||| Childs and Massey, *Proc. Roy. Soc. A*, **142** (1933), 509.

††† Shaw and Snyder, *Phys. Rev.* **58** (1940), 600.

approximations and in the next section we shall do this. It also appears that higher approximations are necessary to account for the angular distribution observed at energies in the neighbourhood of the cross-section minimum for the heavier rare gases.

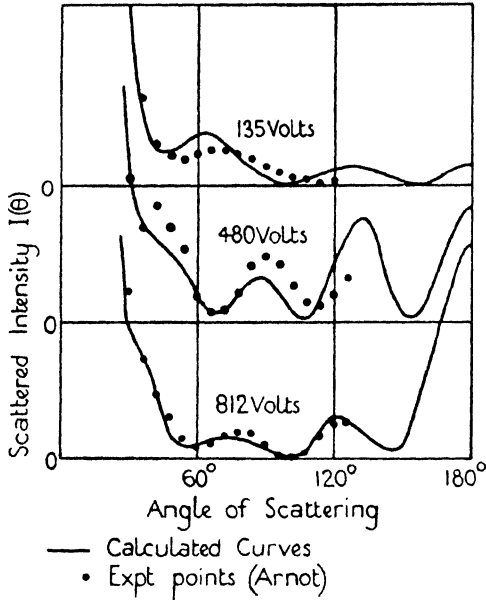


FIG. 32. Comparison of observed and calculated angular distributions of electrons elastically scattered by mercury atoms.

5. Electron exchange in elastic collisions

In Chap. VIII, § 4, the possibility of electron exchange between the atom and the colliding beam was considered. It was shown that an incident electron may either be directly scattered, or may change places with an atomic electron. It was shown also that the probability of the two processes cannot be added; owing to the necessity for using anti-symmetrical wave functions, one must combine the wave amplitudes rather than their intensities.

The possibility of exchange interference was first pointed out by Oppenheimer,[†] who suggested that this was the explanation of the minimum observed in the cross-section velocity curves of the heavier rare gases at very low voltages. In view of the theory discussed in § 3 it is unlikely that this view is correct. For light atoms such as helium and hydrogen, however, exchange interference seems to be of considerable importance in low-velocity collisions.

[†] *Phys. Rev.* **32** (1928), 361.

6. Calculation of effect of electron exchange in elastic scattering by hydrogen and helium

We employ the same notation as that used in Chap. VIII, § 4. It was shown there that the elastic scattering of electrons by atoms of hydrogen and helium may be described by means of two wave functions $F_0(\mathbf{r}_1)$, $G_0(\mathbf{r}_2)$ which have the asymptotic form

$$\begin{aligned} F_0(\mathbf{r}_1) &\sim \exp ikz_1 + r_1^{-1} f_0(\theta_1, \phi_1) \exp ikr_1, \\ G_0(\mathbf{r}_2) &\sim r_2^{-1} g_0(\theta_2, \phi_2) \exp ikr_2. \end{aligned} \quad (7)$$

The differential cross-section for elastic collisions is then

$$\begin{aligned} I(\theta) d\omega &= \frac{1}{4} \{3|f_0 + g_0|^2 + |f_0 - g_0|^2\} d\omega && \text{for hydrogen,} \\ &= |f_0 - g_0|^2 d\omega && \text{for helium.} \end{aligned} \quad (8)$$

For simplicity let us consider the case of hydrogen first. The functions $F_0(\mathbf{r}_1)$, $G_0(\mathbf{r}_2)$ were shown to satisfy the equations

$$\begin{aligned} [\nabla^2 + k^2]F_0(\mathbf{r}_1) &= -\frac{8\pi^2 m \epsilon^2}{\hbar^2} \int \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) \psi_0^*(\mathbf{r}_2) d\tau_2, \\ [\nabla^2 + k^2]G_0(\mathbf{r}_2) &= -\frac{8\pi^2 m \epsilon^2}{\hbar^2} \int \left(\frac{1}{r_2} - \frac{1}{r_{12}} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) \psi_0^*(\mathbf{r}_1) d\tau_1, \end{aligned} \quad (9)$$

where the function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is the wave function for the complete system.

In order to integrate the equations (9) we must assume some approximate form for Ψ on the right-hand side, so that the right-hand side becomes a known function. We know that Ψ may be expanded in the form

$$\Psi = \left(\sum_n + \int \right) F_n(\mathbf{r}_1) \psi_n(\mathbf{r}_2).$$

We may write this $\Psi = F_0(\mathbf{r}_1) \psi_0(\mathbf{r}_2) + \Phi$,

where Φ includes all the scattered waves.

Now Ψ may be expanded in the alternative series

$$\Psi = \left(\sum_n + \int \right) G_n(\mathbf{r}_2) \psi_n(\mathbf{r}_1),$$

as we saw in Chapter VIII. If we expand Φ in the form

$$\Phi = \left(\sum_n + \int \right) G'_n(\mathbf{r}_2) \psi_n(\mathbf{r}_1),$$

then it is to be expected that $G_0 \simeq G'_0$; in other words, the 'exchange' wave is included in Φ . Thus, if we assume for Ψ on the right-hand side of (9)

$$\Psi = F_0(\mathbf{r}_1) \psi_0(\mathbf{r}_2) + G_0(\mathbf{r}_2) \psi_0(\mathbf{r}_1) + \phi, \quad (10)$$

and neglect ϕ , we shall have a fair approximation, which amounts to

neglecting the effect of all waves with wave-length different from that of the incident wave.

If we substitute (10) in (9), we obtain

$$\begin{aligned} & \left[\nabla^2 + k^2 - \frac{8\pi^2 m}{\hbar^2} V_{00}(r_1) \right] F_0(\mathbf{r}_1) \\ &= -\frac{8\pi^2 m \epsilon^2}{\hbar^2} \int \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) G_0(\mathbf{r}_2) \psi_0(\mathbf{r}_1) \psi_0^*(\mathbf{r}_2) d\tau_2 \quad (11a) \end{aligned}$$

and

$$\begin{aligned} & \left[\nabla^2 + k^2 - \frac{8\pi^2 m}{\hbar^2} V_{00}(r_2) \right] G_0(\mathbf{r}_2) \\ &= -\frac{8\pi^2 m \epsilon^2}{\hbar^2} \int \left(\frac{1}{r_2} - \frac{1}{r_{12}} \right) F_0(\mathbf{r}_1) \psi_0(\mathbf{r}_2) \psi_0^*(\mathbf{r}_1) d\tau_1, \quad (11b) \end{aligned}$$

where
$$V_{00}(r_1) = -\epsilon^2 \int \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) |\psi_0(\mathbf{r}_2)|^2 d\tau_2.$$

Changing the variable in G_0 from \mathbf{r}_2 to \mathbf{r}_1 , we obtain, by adding and subtracting (11a) and (11b),

$$\begin{aligned} & \left[\nabla^2 + k^2 - \frac{8\pi^2 m}{\hbar^2} V_{00}(r_1) \right] \{F_0(\mathbf{r}_1) \pm G_0(\mathbf{r}_1)\} \\ &= \mp \frac{8\pi^2 m \epsilon^2}{\hbar^2} \int \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) \{F_0(\mathbf{r}_2) \pm G_0(\mathbf{r}_2)\} \psi_0(\mathbf{r}_1) \psi_0^*(\mathbf{r}_2) d\tau_2. \quad (12) \end{aligned}$$

If we expand $F_0(\mathbf{r}) \pm G_0(\mathbf{r})$ in the form

$$F_0(\mathbf{r}) \pm G_0(\mathbf{r}) = r^{-1} \sum_n f_n^\pm(r) P_n(\cos \theta), \quad (13)$$

then
$$\left\{ \frac{d^2}{dr^2} + k^2 + U_{00} - \frac{n(n+1)}{r^2} \right\} f_n^\pm(r_1) = \mp \int_0^\infty g_n(r_1, r_2) f_n^\pm(r_2) dr_2, \quad (14)$$

where

$$\begin{aligned} g_n(r, r') &= \frac{8\pi m \epsilon^2}{(2n+1)\hbar^2} \psi_0(r_1) r_1 \gamma_n(r_1, r_2) r_2 \psi_0(r_2), \\ \frac{1}{r_1} - \frac{1}{r_{12}} &= \sum \gamma_n(r_1, r_2) P_n \left(\frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1 r_2} \right). \quad (15) \end{aligned}$$

This gives a set of integro-differential equations for the functions f_n . As for the central force problem, the proper solutions have the asymptotic form

$$\sin(kr - \frac{1}{2}n\pi + \eta_n),$$

and the formulae (17) and (18) of Chapter II for the differential and total scattering cross-sections are still valid.

To bring out the effect of the exchange in introducing a change of

phase we may obtain an integral equation for this change in a manner similar to that of § 2.1, Chap. VI. Let F_n be the solution of the equation

$$\left\{ \frac{d^2}{dr^2} + k^2 + U_{00} - \frac{n(n+1)}{r^2} \right\} F_n(r) = 0, \quad (16)$$

which has the asymptotic form

$$F_n \sim \sin(kr - \frac{1}{2}n\pi + \sigma_n). \quad (17)$$

Then we obtain

$$\sin(\eta_n^\pm - \sigma_n) = \mp \int_0^\infty \int_0^\infty F_n(r_1) g_n(r_1, r_2) f_n^\pm(r_2) dr_1 dr_2, \quad (18)$$

where

$$f_n^\pm \sim \sin(kr - \frac{1}{2}n\pi + \eta_n^\pm),$$

and is the exact proper solution of (14).

If both η_n and σ_n are small, i.e. at high electron energies, a good approximation will be obtained by taking

$$F_n(r) = f_n^\pm(r) = \left(\frac{\pi}{2kr} \right)^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr). \quad (19)$$

A less drastic approximation, valid if the effect of exchange, measured by the size of $\eta_n^\pm - \sigma_n$, is small, whereas the direct scattering, measured by σ_n , is not, is given by taking

$$f_n^\pm = F_n, \quad (20)$$

with F_n the exact solution of (16). If neither of these approximations may be made, it is necessary to solve the integro-differential equation numerically. An alternative possibility in this case would be to use a generalization of Hulthén's variation method (Chap. VII, § 6.3).

Before describing the results which have been obtained in investigating the effect of exchange, it is necessary to call attention to a certain defect in the derivation of the equations (12).

Referring to Chap. VIII, § 4.1, we see that the wave function must satisfy the orthogonality relations

$$\begin{aligned} \int \{ \Psi - F_0(\mathbf{r}_1) \psi_0(r_2) \} \psi_0^*(r_2) d\tau_2 &= 0, \\ \int \{ \Psi - G_0(\mathbf{r}_2) \psi_0(r_1) \} \psi_0^*(r_1) d\tau_1 &= 0. \end{aligned} \quad (21)$$

The approximate expression (10) with ϕ neglected does not satisfy these relations. The non-vanishing contribution in each case arises from the zero-order term in the zonal harmonic expansion of F_0 and G_0 . For values of $n \neq 0$ the equations (12) can therefore be regarded as satisfactory in this respect. When $n = 0$, no completely satisfactory way

of meeting the difficulty has been derived, particularly for the symmetrical case. Something further may be done, however, for the antisymmetrical function. The complete wave function describing the collision which has the correct symmetry properties is

$$2^{-1}[\Psi(\mathbf{r}_1, \mathbf{r}_2) - \Psi(\mathbf{r}_2, \mathbf{r}_1)]. \quad (22)$$

This can be written

$$\psi_0(r_1)[F_0(\mathbf{r}_2) - G_0(\mathbf{r}_2)] - \psi_0(r_2)[F_0(\mathbf{r}_1) - G_0(\mathbf{r}_1)]. \quad (23)$$

A partial step towards satisfying (21) will be taken if $F_0(\mathbf{r}) - G_0(\mathbf{r})$ can be made orthogonal to ψ_0 . It was pointed out by Feenberg that,† given any solution $F_0(\mathbf{r}) - G_0(\mathbf{r})$, then the function (22) is unaltered if a constant multiple of ψ_0 is added to this solution. He therefore replaced $F_0(\mathbf{r}) - G_0(\mathbf{r})$ by $F_0(\mathbf{r}) - G_0(\mathbf{r}) + c\psi_0(r)$, where

$$\begin{aligned} c &= \int [F_0(\mathbf{r}) - G_0(\mathbf{r})]\psi_0(r) d\tau \\ &= 4\pi \int f_0^-(r)\psi_0(r)r dr. \end{aligned} \quad (24)$$

This has the effect of replacing $1/r_1$ by $(1/r_{12})_{00}$, where

$$\left(\frac{1}{r_{12}}\right)_{00} = \int \frac{|\psi_0(r)|^2}{r_{12}} d\tau. \quad (25)$$

An alternative procedure, which may be employed for all cases which arise, is to obtain the integro-differential equations in the same way as the Fock equations‡ for the self-consistent field of an atom with exchange included. These equations are strictly valid only for closed states but, by regarding the continuous state of the colliding electrons as the limit of a discrete state, they may be employed for the scattering problem. It must be remembered, however, that although provision exists in this method for satisfying certain orthogonality conditions, these are not, in this application, quite the correct ones. Thus, taking the example of the hydrogen atom, the application of the Fock method gives an equation for F^\pm where

$$2^{-1}[\Psi(\mathbf{r}_1, \mathbf{r}_2) \pm \Psi(\mathbf{r}_2, \mathbf{r}_1)] = 2^{-1}[\psi_0(r_1)F^\pm(\mathbf{r}_2) - \psi_0(r_2)F^\pm(\mathbf{r}_1)].$$

Provision is thereby made for ψ_0 to be orthogonal to F^\pm , but this makes the ground state function of the hydrogen atom orthogonal to one representing, *not* a continuous state of the atom, but of the negative hydrogen ion. Until a comparison has been made between the different ways of dealing with the orthogonality question, we cannot be sure which is the best.

† *Phys. Rev.* **40** (1932), 40.

‡ Fock, *Zeits. f. Physik*, **61** (1930), 126. See also Mott and Sneddon, *Wave Mechanics and its Applications*, Chap. VI, § 28.

6.1. Numerical applications to elastic scattering

The first attempts to allow in detail for the effects of exchange in elastic scattering were made by Massey and Mohr† for hydrogen and helium, using essentially the approximations (19) and (20). They found that the effect should become appreciable for electron energies below 15 e.V. in helium and 5 e.V. in hydrogen. It was suggested that much of the failure of the Faxén-Holtmark theory at low energies in helium (see p. 212 and Fig. 31) was due to exchange. This was confirmed by

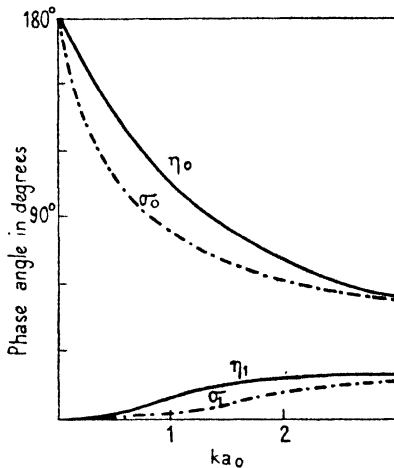


FIG. 33. Phase shifts in electron scattering by helium calculated with (η) and without (σ) inclusion of exchange.

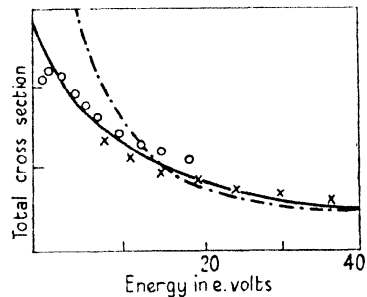


FIG. 34. Comparison of observed and calculated total cross-sections for collisions of electrons with helium atoms.

- Calculated with inclusion of exchange.
- - - - Calculated without inclusion of exchange.
- Experimental points (Ramsauer and Kollath).
- × Experimental points (Normand).

Allis and Morse,‡ who obtained accurate numerical solutions of the integro-differential equations (12) for $n = 0$ and $n = 1$ in the form appropriate to helium, orthogonality being allowed for by Feenberg's method. The effect of exchange in modifying the phase shifts is illustrated in Fig. 33. It will be seen that for low energies, below 15 e.V., the phase η_1 is increased substantially as is η_0 . For the latter, however, the increase is to values beyond 90° . The net effect is to increase the importance of the first-order scattering relative to the zero order, giving a less uniform angular distribution, in agreement with the experimental requirements. A comparison of the observed and calculated angular distributions and cross-sections is given in Figs. 34 and 35. It will be seen that, while much better agreement is obtained when exchange is

† *Proc. Roy. Soc. A*, **132** (1931), 605; **136** (1931), 289; and **139** (1932), 187.

‡ *Phys. Rev.* **44** (1933), 269.

included, there is still a discrepancy at small angles. This is probably due to polarization, an effect which will be discussed in the next section.

Morse and Allis also discussed a schematic model to represent the case of more complex atoms and from it were able to produce evidence suggesting that exchange effects become less and less important the

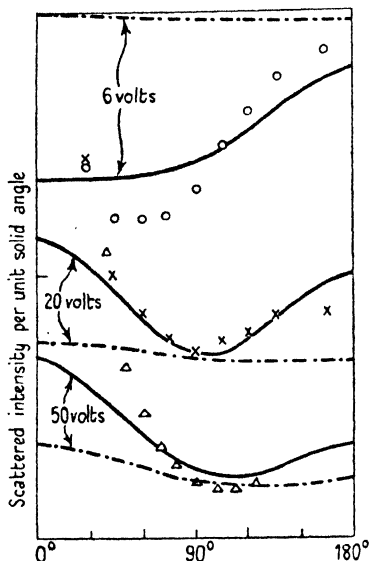


FIG. 35. Comparison of observed and calculated angular distributions for scattering of electrons by helium atoms.

- Calculated with inclusion of exchange.
- - - - Calculated without inclusion of exchange.
- Experimental points for 6 volt electrons (Ramsauer and Kollath).
- × Experimental points for 20 volt electrons (Ramsauer and Kollath).
- △ Experimental points for 50 volt electrons (Bullard and Massey).

Except for 50 volt electrons, absolute values are compared. For 50 volt electrons scales are adjusted so that theory (with exchange) and experiment agree at 80° .

heavier the atom. The only calculations of a detailed character which have been carried out for a heavier atom are those of Bates and Massey† for oxygen, using the Fock formulation. As they also included an empirical polarization term, it is difficult to obtain from their results any evidence as to the relative importance of exchange.

7. The effect of polarization

So far we have neglected all consideration of the effect of the inelastically scattered waves on the elastic scattering. This results in a more

† *Proc. Roy. Soc. A*, 192 (1947), 1.

rapid increase of scattering with diminishing angle at small angles of scattering. A detailed theory would be very complicated, but Massey and Mohr† have carried the analysis far enough to render the explanation a plausible one for effects of this kind, observed for electrons with energies of 100 e.V. or more, scattered in helium and hydrogen.

Let us consider for simplicity the scattering of electrons by hydrogen atoms. Referring to Chap. VII, § 1, we see that the function $F_0(\mathbf{r}_1)$, describing the elastic scattering, satisfies the equation

$$(\nabla^2 + k^2)F_0(\mathbf{r}_1) = \frac{8\pi^2m}{h^2} \sum_n V_{0n}(\mathbf{r}_1)F_n(\mathbf{r}_1), \tag{26}$$

where
$$V_{0n} = \epsilon^2 \int \left(\frac{1}{r_{12}} - \frac{1}{r_1} \right) \psi_0^*(r_2) \psi_n(r_2) d\tau_2. \tag{27}$$

It was shown also that, within the accuracy of Born's approximation,

$$F_0 = e^{ik\mathbf{n}_0 \cdot \mathbf{r}_1} - \frac{2\pi m}{h^2} \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} \exp\{ik|\mathbf{r}_1 - \mathbf{r}_3| + ik\mathbf{n}_0 \cdot \mathbf{r}_3\} V_{00}(r_3) d\tau_3, \tag{28}$$

$$F_n = -\frac{2\pi m}{h^2} \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} \exp\{ik_n|\mathbf{r}_1 - \mathbf{r}_3| + ik\mathbf{n}_0 \cdot \mathbf{r}_3\} V_{n0}(r_3) d\tau_3. \tag{29}$$

To obtain a second approximation to F_0 we substitute (28) and (29) on the right-hand side of (26) to give

$$(\nabla^2 + k^2)F_0 = \frac{8\pi^2m}{h^2} V_{00} e^{ik\mathbf{n}_0 \cdot \mathbf{r}_1} - \frac{16\pi^3m^2}{h^4} \sum_n V_{0n}(\mathbf{r}_1) \int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} \exp\{ik_n|\mathbf{r}_1 - \mathbf{r}_3| + ik\mathbf{n}_0 \cdot \mathbf{r}_3\} V_{n0}(r_3) d\tau_3. \tag{30}$$

In order to sum the series involved we now restrict ourselves to such velocities of impact that $k_n \simeq k$ for all values of n which contribute appreciably. We may then use the result

$$\sum_n V_{0n}(\mathbf{r}_1) V_{n0}(r_3) = \int V(\mathbf{r}_2, \mathbf{r}_3) V(\mathbf{r}_2, \mathbf{r}_1) |\psi_0(r_2)|^2 d\tau_2, \tag{31}$$

where
$$V(\mathbf{r}_2, \mathbf{r}_3) = \epsilon^2 \left(\frac{1}{r_{23}} - \frac{1}{r_3} \right).$$

This gives
$$(\nabla^2 + k^2)F_0(\mathbf{r}_1) = \frac{8\pi^2m}{h^2} e^{ik\mathbf{n}_0 \cdot \mathbf{r}_1} \{V_{00} + v_{00}\}, \tag{32}$$

where

$$v_{00} = -\frac{2\pi m}{h^2} \iint \exp\{ik(\rho_3 + \mathbf{n}_0 \cdot \rho_3)\} V(\rho_2 + \mathbf{r}_1, \mathbf{r}_1) V(\rho_2 + \mathbf{r}_1, \rho_3 + \mathbf{r}_1) \times |\psi_0(\rho_2 + \mathbf{r}_1)|^2 \rho_3^{-1} d\rho_2 d\rho_3. \tag{33}$$

In obtaining this form for v_{00} the origin of coordinates has been changed

† *Proc. Roy. Soc. A*, 146 (1934), 880.

to the point 1, the position vectors of the points 2 and 3 relative to this origin being denoted by ρ_2 and ρ_3 .

From the form of (32) it is clear that v_{00} represents an extra scattering potential which must be added to the static potential of the atom. As it stands it includes, not only the effect of the inelastically scattered waves, but also the second approximation to the solution of the equation

$$(\nabla^2 + k^2)F_0 = \frac{8\pi^2 m}{\hbar^2} V_{00} F_0. \quad (34)$$

The true polarization potential v_p will be obtained by subtracting this contribution, which we call u_{00} , from v_{00} . It may easily be shown that

$$u_{00} = -\frac{2\pi m}{\hbar^2} V_{00} \int V_{00}(|\rho_3 + \mathbf{r}_1|) \rho_3^{-1} \exp\{ik(\rho_3 + \mathbf{n}_0 \cdot \rho_3)\} d\rho_3. \quad (35)$$

It is clear that $v_p = v_{00} - u_{00}$ is a very complicated function of \mathbf{r}_1 and k . Massey and Mohr† calculated the zero and first-order terms in the harmonic expansion of v_p and found good convergence in the separate, still very complicated, contributions from these two. For large values of r they showed that

$$v_p \sim -\frac{\epsilon^2 a_0}{2k} \left[\frac{2i}{r^3} + \frac{1 - 3 \cos \theta}{r^4 k} \left\{ 1 - \frac{e^{2ikr}}{(1 + k^2 a_0^2)^3} \right\} + O\left(\frac{1}{r^5}\right) \right]. \quad (36)$$

The second term is of the nature of a dynamic polarization, but the first, which is purely imaginary, corresponds to an absorption potential. It may, perhaps, be interpreted as due to the loss of electrons from the incident beam by inelastic scattering. In any case it has a very marked effect on the small angle scattering as it falls off so slowly with distance. It leads to a differential cross-section which tends logarithmically to infinity at very small angles. Fig. 36 illustrates the comparison of the observed angular distributions for electrons with energies between 75 and 350 e.V. scattered by helium, with the theoretical ones obtained from the formula

$$I(\theta) = \frac{4\pi^2 m^2}{\hbar^4} \left| \int e^{ik(\mathbf{n}_0 - \mathbf{n}_1) \cdot \mathbf{r}} (V_{00} + v_p) d\tau \right|^2. \quad (37)$$

The comparison has been effected by adjusting the ordinates of experimental and theoretical curves to agree at 60° for 350 e.V. electrons. It will be seen that the agreement is quite good and very much better at small angles than when v_p is ignored. The validity of the theory has been confirmed to even smaller angles (to 2°) in helium. Thus Whiddington‡ finds that, between 5° and 2° in helium, the scattered intensity for

† Loc. cit.

‡ *Nature*, **133** (1934), 685.

200 volt electrons doubles. According to Born's first approximation there should be little change between these angles, but the effect of v_p is to produce very nearly the observed increase.

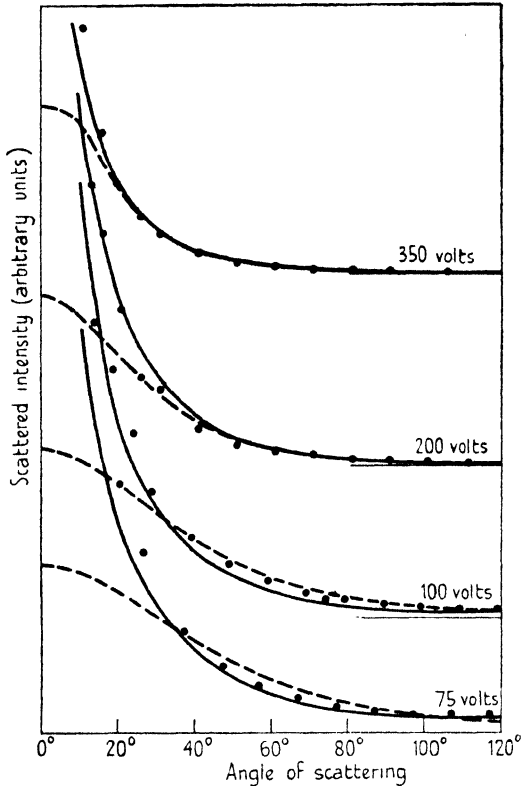


FIG. 36. Comparison of observed and calculated angular distributions for scattering of electrons by helium atoms.

- Calculated by Born's approximation.
- Calculated taking polarization and distortion into account.
- Experimental points (Hughes, McMillen, and Webb).

Similar agreement is found for hydrogen, assuming that the molecule behaves like two atoms. The ratio of the polarization amplitude to that given by Born's first approximation is a function of Z/k , where Z is the effective nuclear charge. As a result the effect should be apparent at higher energies in helium than in hydrogen, and this is observed.

Unfortunately it has not proved possible to extend the theory to cover lower energy impacts, but it is probable that the polarization effect is important at small angles down to very low energies.

XI

INELASTIC COLLISIONS OF ELECTRONS WITH ATOMS

WE limit ourselves in this chapter, except where otherwise stated, to the case of fast electrons ($v \gg \epsilon^2/h$); the first Born approximation is then sufficient. This introduces sufficient simplification to enable the calculation of the stopping-power of any material, the probability of ionization of an inner level of an atom, etc., to be carried out with sufficient accuracy to make possible a comparison with experiment. We shall first consider in some detail the case of inelastic collisions with hydrogen and helium atoms. It will then be found possible to generalize the results obtained for these simple cases to more complicated atoms.

1. General formulae

Consider the collision of an electron with an atom in which the atom is raised from the state m to state n by the impact. If E_m, E_n are the energies of the two atomic states and v, v_{mn} the initial and final velocities of the colliding electron, we have

$$\frac{1}{2}m(v^2 - v_{mn}^2) = E_n - E_m. \quad (1)$$

It was shown in Chapter VIII that, within the range of validity of the first approximation of Born's theory, the differential cross-section corresponding to the collision is given by

$$I_{mn}(\theta) d\omega = \frac{4\pi^2 m^2}{h^4} \frac{k_{mn}}{k} \left| \iint V(\mathbf{r}, \mathbf{R}) \exp\{i(k_{mn} \mathbf{n}_1 - k \mathbf{n}_0) \cdot \mathbf{R}\} \psi_n^*(\mathbf{r}) \psi_m(\mathbf{r}) d\mathbf{r} d\mathbf{R} \right|^2 d\omega, \quad (2)$$

where $k\hbar \mathbf{n}_0/2\pi, k_{mn}\hbar \mathbf{n}_1/2\pi$ are the initial and final momentum vectors of the colliding electron, and ψ_m, ψ_n are the initial and final atomic wave functions of the atom. The interaction energy V is the Coulomb interaction between the incident and atomic electrons, $\epsilon^2/|\mathbf{r} - \mathbf{R}|$.†

We note that the probability of a transition from one state to another of a different term system (such as a singlet-triplet transition in helium) is zero to this approximation, since the perturbing potential V is symmetrical in the coordinates of the atomic electrons, whereas the wave functions ψ_n, ψ_m will have different symmetry properties. The integral in (2) will therefore vanish. This result is in agreement with experi-

† The effect of the Coulomb interaction between the incident electron and the atomic nucleus vanishes on account of the orthogonal properties of the atomic wave functions.

ment for fast collisions, but not for slow collisions. The discrepancy is due to neglect of electron exchange, as is explained in § 5 of this chapter.

If the colliding electron ionizes the atom, the state n will lie in the continuous spectrum. We distinguish a level of the continuous spectrum by a quantity κ related to the energy of the level by the formula

$$E_\kappa = \kappa^2 \hbar^2 / 8\pi^2 m. \tag{3}$$

The normalization of continuous wave functions is discussed in Chap. XIV, § 2.1. We normalize in such a way that the differential cross-section given by (2), multiplied by $d\kappa$, corresponds to a range of energy such that κ lies between κ and $\kappa + d\kappa$; we must thus have

$$\int_0^\infty \psi_\kappa(\mathbf{r}) \psi_{\kappa'}(\mathbf{r}) d\mathbf{r} = \delta(\kappa - \kappa'). \tag{4}$$

The differential cross-section corresponding to the excitation of a set of continuous energy-levels lying between κ and $\kappa + d\kappa$ is then given by

$$I_{m\kappa}(\theta) d\kappa = \frac{4\pi^2 m^2}{\hbar^4} \frac{k_{m\kappa}}{k} \left| \int \int V \exp\{i(k_{m\kappa} \mathbf{n}_1 - k \mathbf{n}_0) \cdot \mathbf{R}\} \psi_\kappa^* \psi_m d\mathbf{r} d\mathbf{R} \right|^2 d\kappa. \tag{5}$$

1.1. *Introduction of momentum variables*

For most purposes it is convenient to change from angular to momentum variables. The vector

$$(k_{mn} \mathbf{n}_1 - k \mathbf{n}_0) \hbar / 2\pi$$

is the change of momentum of the incident electron. If we choose the axis of a system of polar coordinates along this vector, we have†

$$\exp\{i(k_{mn} \mathbf{n}_1 - k \mathbf{n}_0) \cdot \mathbf{R}\} = \exp(iKX), \tag{6}$$

where

$$\begin{aligned} K &= |k_{mn} \mathbf{n}_1 - k \mathbf{n}_0| \\ &= (k_{mn}^2 + k^2 - 2kk_{mn} \cos \theta)^{\frac{1}{2}}. \end{aligned} \tag{7}$$

The scalar K denotes the magnitude of the momentum change when an electron is scattered through an angle θ . Since

$$K dK = kk_{mn} \sin \theta d\theta,$$

we have, for the cross-section for momentum change between K and $K + dK$,

$$I_{mn}(K) dK = \frac{8\pi^2 m^2}{\hbar^4} \frac{K dK}{k^2} \left| \int \int V e^{iKX} \psi_m \psi_n^* d\mathbf{r} d\mathbf{R} \right|^2. \tag{8}$$

† Compare Chap. VII, § 1. We write X in place of Z to avoid confusion with the effective nuclear charge Z .

This expression for $I_{mn}(K)$ may be simplified by performing the integration over the coordinates of the colliding electron. Let the Z atomic electrons be denoted by suffixes 1, 2, ..., Z . Then

$$\int V e^{iKX} d\mathbf{R} = \epsilon^2 \sum_{s=1}^{s=Z} \int \frac{e^{iKX}}{|\mathbf{R}-\mathbf{r}_s|} d\mathbf{R}.$$

Making use of the formula†

$$\int \frac{\exp(iK\mathbf{n} \cdot \mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = \frac{4\pi}{K^2} e^{iK\mathbf{n} \cdot \mathbf{r}},$$

we have

$$\int V e^{iKX} d\mathbf{R} = \frac{4\pi\epsilon^2}{K^2} \sum_{s=1}^{s=Z} e^{iKx_s}. \quad (9)$$

Substituting in (8), we then obtain finally

$$I_{mn}(K) dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 \hbar^4} \frac{dK}{K^3} |\epsilon_{mn}(K)|^2, \quad (10)$$

where

$$\epsilon_{mn}(K) = \sum_{s=1}^{s=Z} \int e^{iKx_s} \psi_m \psi_n^* d\mathbf{r}. \quad (11)$$

The effective cross-section corresponding to the mn transition will be obtained by integrating the differential cross-section (10) between the limits of allowed momentum change, i.e.

$$Q_{mn}(k) = \int_{K_{\min}}^{K_{\max}} I_{mn}(K) dK. \quad (12)$$

In view of their importance in the following sections we will examine these limits for the particular case of fast electrons. It is easily seen that

$$K_{\max} = k + k_{mn},$$

$$K_{\min} = k - k_{mn},$$

and that, as a consequence of the energetic relation (1),

$$k^2 = k_{mn}^2 + 8\pi^2 m(E_n - E_m)/\hbar^2.$$

For the case of fast collisions we have, then,

$$k_{mn} \simeq k - 4\pi^2 m(E_n - E_m)/\hbar^2 k,$$

and so

$$k + k_{mn} \simeq 2k$$

$$k - k_{mn} \simeq 4\pi^2 m(E_n - E_m)/\hbar^2 k. \quad (13)$$

† Bethe, *Ann. der Phys.* 5 (1930), 325.

2. Calculation of differential cross-sections for hydrogen and helium. Angular distributions of inelastically scattered electrons

2.1. Excitation of discrete levels

To calculate the differential cross-section $I_{mn}(K) dK$ we require the wave functions of the states m, n . In all cases we suppose the initial level to be the ground state, for which we use the suffix 0. Also we write k_n for k_{0n} . The wave functions for the ground states† are

$$\begin{aligned} \psi_0 &= (\pi a_0^3)^{-1/2} e^{-r/a_0} && \text{for hydrogen,} \\ &= Z^3 (\pi a_0^3)^{-1/2} e^{-Z(r_1+r_2)/a_0} && \text{for helium, with } Z = 1.69. \end{aligned} \quad (14)$$

For the higher states of hydrogen-like atoms the wave functions ψ_{nlm} take the form‡

$$\begin{aligned} \psi_{nlm} &= N_{nlm} r_1^l L_{n+l}^{2l+1} \left(\frac{2r_1 Z}{na_0} \right) \exp \left(-\frac{Zr_1}{na_0} \right) P_l^m(\cos \theta_1) e^{\pm im\phi_1}, \\ N_{nlm}^2 &= \frac{2^{2l}}{n\pi} (2l+1) \frac{(l-m)!(n-l-1)!}{(l+m)! \{(n+l)!\}^3} \left(\frac{Z}{na_0} \right)^{2l+3}, \end{aligned} \quad (15)$$

where Z is the nuclear charge; for helium it is necessary to make certain approximations, as in the case of the ground state. It has been shown by Eckart§ that a good approximation to the wave function of an excited state of helium (other than an S state) is obtained by taking a symmetrical combination of the product of two wave functions, one representing the ground state of an electron in the field of a charge 2, the other the excited state of an electron in the field of a charge 1.|| Hence, if we write

$$\psi_{nlm}(Z|r)$$

for the wave function of a single electron in the nlm state in the field of a charge $Z\epsilon$, we may take, as a sufficiently good approximation for the wave function of an excited singlet state of helium, the form

$$2^{-1} \{ \psi_0(2|r_1) \psi_{nlm}(1|r_2) + \psi_0(2|r_2) \psi_{nlm}(1|r_1) \}, \quad (16)$$

the two electrons being distinguished by the numerals 1, 2.

On substitution of the wave functions (16), (15), and (14) in the expression (10) for the differential cross-section, we see that

$$\epsilon_{nlm}(K) = \alpha \int \psi_0(Z|r') \psi_{nlm}^*(Z'|r') e^{iKx'} d\tau',$$

† Cf. Chap. IX, § 3.

‡ Sommerfeld, *Introduction to Wave Mechanics*, p. 59.

§ *Phys. Rev.* **36** (1930), 878.

|| For S states a more complicated wave function must be used. See Massey and Mohr, *Proc. Roy. Soc. A*, **140** (1933), 613.

where

$$\begin{aligned} \alpha &= 1, & Z = Z' = 1 & \quad \text{for hydrogen,} \\ \alpha &= 2^{\frac{1}{2}}, & Z = 1.69, Z' = 1 & \quad \text{for helium.} \end{aligned}$$

The value of this integral may be calculated† for all nlm , and we find that

$$\begin{aligned} \epsilon_{nlm}(K) &= 2^{2l+3} n^{l+1} (2l+1)! Z^{\frac{1}{2}} (l+1)! \{(n-l-1)!\}^{\frac{1}{2}} \{(n+l)!\}^{-\frac{1}{2}} (Ka_0)^l \times \\ &\times \frac{\{(nZ-1)^2 + 4\zeta^2\}^{\frac{1}{2}(n-l-3)}}{\{(nZ+1)^2 + 4\zeta^2\}^{\frac{1}{2}(n+l+3)}} [(nZ+1)\{(nZ-1)^2 + 4\zeta^2\} C_{n-l-1}^{l+\frac{3}{2}}(x) - \\ &- 2nZ\{(nZ-1)^2 + 4\zeta^2\}^{\frac{1}{2}} \{(nZ+1)^2 + 4\zeta^2\}^{\frac{1}{2}} C_{n-l-2}^{l+\frac{3}{2}}(x) + \\ &+ (nZ-1)\{(nZ+1)^2 + 4\zeta^2\} C_{n-l-3}^{l+\frac{3}{2}}(x)], \end{aligned} \quad (17)$$

where

$$\begin{aligned} x &= (n^2 Z^2 - 1 + 4\zeta^2) [\{(nZ+1)^2 + 4\zeta^2\} \{(nZ-1)^2 + 4\zeta^2\}]^{-\frac{1}{2}}, \\ \zeta &= \frac{1}{2} Kna_0. \end{aligned} \quad (18)$$

The coefficients C_s^ν are defined in terms of the expansion

$$(1 - 2ut + u^2)^{-\nu} = \sum_{s=0}^{\infty} C_s^\nu(t) u^s.$$

The expressions for these coefficients for $s = 0, 1, 2, 3$ are

$$\begin{aligned} C_0^\nu(x) &= 1, & C_1^\nu(x) &= 2\nu x, & C_2^\nu(x) &= \nu\{(2\nu+1)x^2 - 1\}, \\ C_3^\nu(x) &= \nu\{2(\nu+1)x^2 - 1\}. \end{aligned} \quad (19)$$

In order to examine the general features of the formulae we will consider the 2 and 3 quantum levels only. In Fig. 37 the angular distributions of electrons of 200 e.V. incident energy scattered after exciting various quantum levels of helium are shown. For purposes of comparison the distributions corresponding to elastic scattering are given. It is clear from these figures that:

(a) The excitation of the optically allowed levels takes place with much greater probability than that of the optically disallowed.

(b) The probability falls off very rapidly with increase in the angle of scattering. At small angles the excitation of the 2^1P level takes place with greater probability than an elastic collision, but the reverse is the case at large angles.

(c) The inelastic scattering is negligible when

$$Ka_0 \gg Z.$$

The reason for this is clearly seen by reference to the formulae (17), (18), (19), which show that, when $Ka_0 \gg Z$, the excitation probability

† Massey and Mohr, *Proc. Roy. Soc. A*, **132** (1931), 605.

falls off as K^{-12} , K^{-14} , K^{-16} for S , P , D states respectively. Since $Z\epsilon^2/2a_0$ is the ionization potential of the atom, we may say that the differential cross-section is negligible when

$$K \gg V_i/\epsilon^2,$$

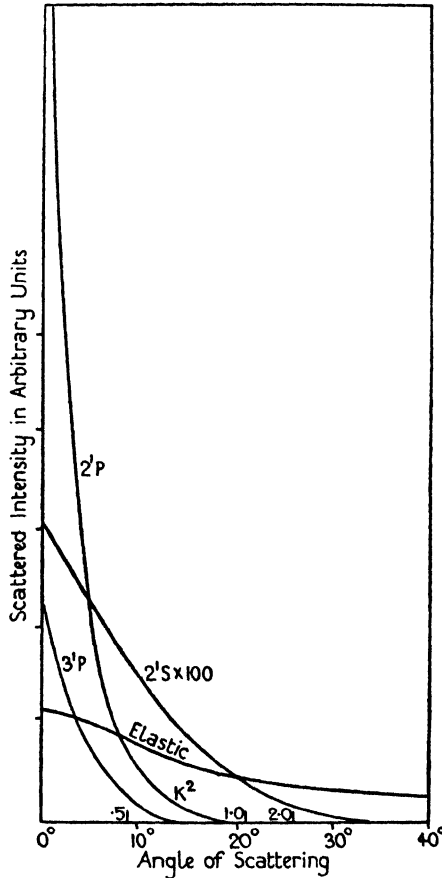


FIG. 37. Angular distribution of electrons of 200 e.V. incident energy scattered by helium atoms after exciting various levels.

K^2 is given also for the $2'P$ transition, in atomic units.

V_i being the ionization potential of the atom concerned. This result may be generalized immediately for any atom.

In Table I the values of $2\pi I_{0n}(\theta)$ are given, for various velocities of impact and angles of scattering, for a number of inelastic collisions in helium. It is unlikely, on theoretical grounds, that the formulæ obtained by the use of the first approximation of Born's theory can be

TABLE I
Cross-section ($2\pi I(\theta)$) in Units of πa_0^2
Angle of Scattering

<i>State excited</i>	0°	5°	10°	20°	30°	40°
100 volts	0.99	0.98	0.92	0.79	0.61	0.45
1 ¹ S 200 „	0.99	0.97	0.88	0.65	0.41	0.25
400 „	0.99	0.95	0.77	0.45	0.22	0.10
100 volts	0.126	0.120	0.086	0.049	0.020	0.0063
2 ¹ S 200 „	0.155	0.126	0.086	0.024	0.0039	0.068 ₃
400 „	0.166	0.120	0.057	0.0051	0.086 ₃	0.03 ₄
100 volts	7.8	4.4	1.78	0.32	0.056	0.013
2 ¹ P 200 „	17.7	4.5	0.99	0.068	0.0088	0.07 ₃
400 „	39	2.6	0.33	0.009	0.0003	0.02 ₃
100 volts	1.84	1.20	0.45	0.103	0.021	0.0043
3 ¹ P 200 „	4.5	1.33	0.24	0.027	0.0025	0.028 ₃
400 „	9.7	0.81	0.084	0.0035	0.014 ₃	0.08 ₅
100 volts	0.0109	0.0098	0.0070	0.0028	0.07 ₃	0.014 ₃
3 ¹ D 200 „	0.0132	0.010	0.0052	0.086 ₃	0.08 ₄	0.07 ₅
400 „	0.0142	0.0094	0.0023	0.011 ₃	0.03 ₅	0.01 ₆
100 volts	0.68	0.46	0.215	0.043	0.0092	0.0020
4 ¹ P 200 „	1.71	0.52	0.131	0.011	0.0012	0.013 ₃
400 „	3.7	0.33	0.048	0.0015	0.06 ₄	0.04 ₅

regarded as very accurate, even for impacts of 200 volt electrons; but comparison with the available experimental material shows that good general agreement is obtained.†

Experiments in helium have been carried out by Dymond and Watson‡ using 200 volt electrons, by McMillen§ using 100 volt electrons, and by Mohr and Nicoll|| using 54, 83, 120, and 196 volt electrons. The observed angular distributions of electrons which have excited the 2P level agree well with the theoretical, as may be seen by reference to Fig. 38, in which the comparison is made. For the collisions of the lower velocity electrons (less than 80 volts) the agreement is not good at large angles of scattering, but this failure is to be expected (cf. § 5.2). Comparison of theoretical††

† For a detailed discussion see Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chap. III.

‡ *Proc. Roy. Soc. A*, **122** (1929), 571.

§ *Phys. Rev.* **36** (1930), 1034.

|| *Proc. Roy. Soc. A*, **138** (1932), 229.

†† Detailed calculations for atomic hydrogen have been carried out by Elsasser (*Zeits. f. Physik*, **45** (1926), 522), Bethe (*Ann. der Phys.* **5** (1930), 325), and Goldstein (*Thèses*, Paris (1932)).

and observed† results for electrons scattered inelastically in hydrogen reveals the same behaviour. (The theory refers to atomic hydrogen, the experiments to the molecule, but at the velocities concerned little difference in behaviour of the two is to be expected.)

The observed relative magnitudes of the inelastic and elastic scattering probabilities also agree quite well with the calculated values. It has

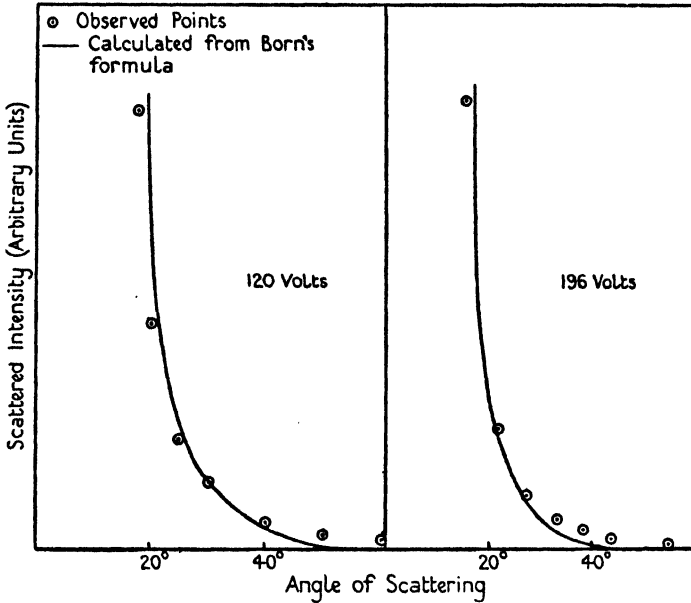


FIG. 38. Angular distributions of electrons scattered inelastically by helium atoms.

not yet proved possible to observe electrons which have excited optically forbidden transitions in helium or hydrogen, which shows that the intensity of such excitation is small. Experiments conducted by Whiddington and Roberts‡ and by van Atta,§ in which only non-deviated electrons were examined, exhibit this result very clearly. In Fig. 39 an experimental velocity distribution curve of non-deviated electrons of 200 volts incident velocity through helium is illustrated. Electrons which have excited the 2^1P , 3^1P , and 4^1P levels can be distinguished clearly, but no other inelastically scattered electrons (except those which have made ionizing collisions) can be detected. The relative intensities of excitation of the various P levels is also in good agree-

† Harnwell, *Phys. Rev.* **34** (1929), 661; Hughes and McMillen, *ibid.* **41** (1932), 39; Mohr and Nicoll, *Proc. Roy. Soc. A*, **138** (1932), 469.

‡ *Proc. Leeds Phil. Soc.* **2** (1931), 201.

§ *Phys. Rev.* **38** (1931), 876.

ment with theory. In van Atta's measurements only electrons scattered between angles of 0° and $1^\circ 40'$ were collected, and the observed variation of intensity with velocity of electrons which have excited the 2^1P level is in agreement with that given in Table I, a steady increase of intensity with velocity being observed.

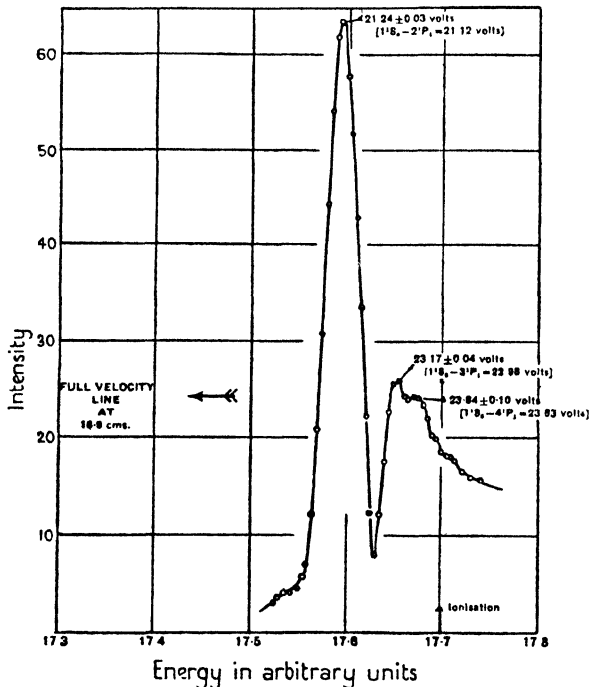


FIG. 39. Velocity analysis of non-deviated electrons of 120 volts incident energy scattered by helium atoms.

We find, then, a close agreement between theory and experiment when this is to be expected. Further comparison with experiment will be discussed in § 3 in connexion with the calculation of total cross-sections. We must now consider the calculation of the differential cross-sections corresponding to the excitation of levels in the continuous spectrum (i.e. to ionization of the atom).

2.2. Excitation of continuous levels. Ionization

In any experiment in which ionizing collisions are investigated it is impossible to distinguish between scattered and ejected electrons. If electrons having a definite energy E' are measured after the collision, these will be composed, not only of electrons scattered after losing

energy $E - E'$, but also of electrons ejected from the atom with energy E' , E being the energy of the incident electron. In order to compare the results of experiment with observation it is, in general, necessary to allow for the interference of the two sets of electron waves,† but under certain conditions this interference may be small and we may apply an approximate theory which does not take account of the interference. For the calculation of the probability of ionization by electrons of a given velocity, the inclusion of interference effects does not alter the result, so we will simply develop the theory without taking such effects into account. We will see later the conditions under which the interference may be neglected in discussing angular and velocity distributions of the electrons.

The wave function corresponding to a state κ of the continuous spectrum in which the electron is moving in the direction with polar angles (χ, ψ) in the field of a charge $Z\epsilon$ is given by‡

$$\psi_{\kappa}^* = \frac{\kappa}{2\pi} \left(\frac{n}{1 - e^{-2\pi n}} \right)^{\frac{1}{2}} \frac{e^{i\kappa r}}{\Gamma(1 - in)} \int_0^{\infty} u^{-in} e^{-u} J_0\{2(i\kappa\xi u)^{\frac{1}{2}}\} du,$$

where

$$\xi = r(1 + \cos\Theta),$$

$$\cos\Theta = \cos\theta \cos\chi + \sin\theta \sin\chi \cos(\phi - \psi),$$

and

$$n = Z/\kappa a_0. \tag{20}$$

For hydrogen we take $Z = 1$ in (20); it is difficult to obtain a satisfactory wave function for helium. A rough approximation is to take the wave function of the excited electron as hydrogenic in form and corresponding to a nuclear charge 1.69 (the effective nuclear charge of the ground state). This function has the merit of being orthogonal to the ground state wave function: in any case the error made will probably not be great for the high velocities of impact for which Born's first approximation is valid.

Using these wave functions in the formula (10), we find for the differential cross-section corresponding to ejection of the atomic electron with energy E_{κ} in the direction (χ, ψ) relative to the direction of incidence of the exciting electron, into the cone of solid angle $d\sigma$, the incident electron being scattered in the direction (θ, ϕ) into the cone of

† Cf. Chap. VIII, § 4.3.

‡ Sommerfeld, *Ann. der Physik*, 11 (1931), 257. The normalization is such that ψ_{κ}^* represents an outgoing plane wave together with an outgoing spherical wave. (Cf. Chap. XIV, § 2.1.)

solid angle $d\omega$, the expression†

$$I_{\kappa} d\sigma d\omega d\kappa = \frac{2^8 \mu^6 k_{\kappa}}{\pi a_0^2 k K^2} \frac{\exp[-(2\mu/\kappa)\arctan\{2\mu\kappa/(\mu^2 + K^2 - \kappa^2)\}]}{(1 - e^{-2\pi\mu/\kappa})(\mu^2 + K^2 + \kappa^2 - 2K\kappa \cos \delta)^4} \times \\ \times \{(K - \kappa \cos \delta)^2 + \mu^2\} / \{(\mu^2 + K^2 - \kappa^2)^2 + 4\mu^2\kappa^2\} d\sigma d\omega d\kappa, \quad (21)$$

where δ is the angle between the vector $k\mathbf{n}_0 - k_{\kappa}\mathbf{n}_1$ (the change of momentum of the incident electron) and the direction (χ, ψ) , $\mu = Z/a_0$.

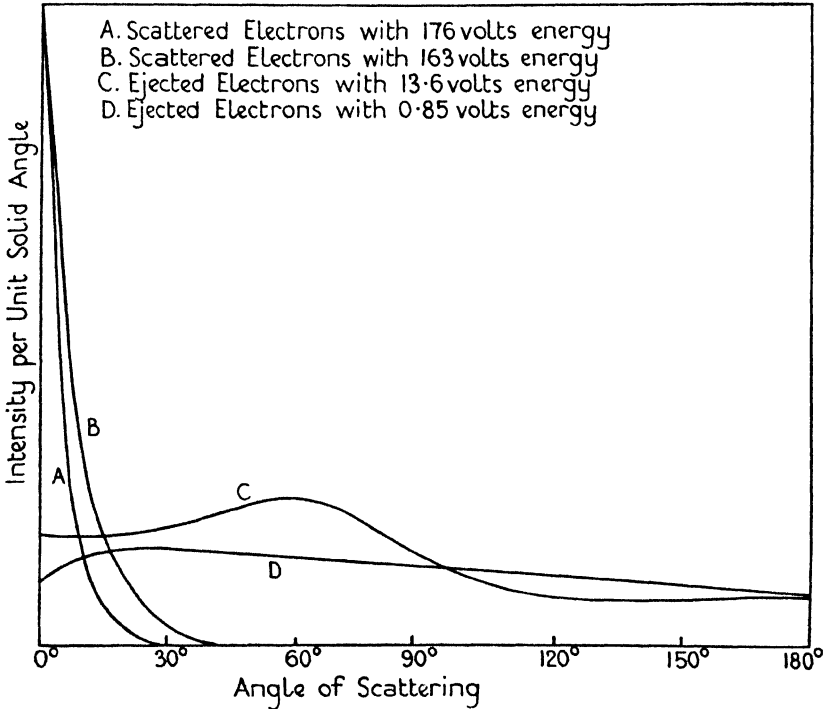


FIG. 40. Angular distributions of scattered and ejected electrons corresponding to electrons of 200 volts incident energy.

We note that the expression (21) is a maximum when $\delta = 0$, corresponding to the conservation of momentum in the collision between the incident and atomic electrons. To obtain the angular distribution of the ejected electrons it is necessary to integrate (21) over all angles of scattering of the colliding electron. This can only be done numerically. Two typical angular distributions are illustrated in Fig. 40. The maxima are given by the condition

$$k^2 + \kappa^2 - 2k\kappa \cos \chi = k_{\kappa}^2$$

which corresponds to the conservation of momentum.

† Massey and Mohr, *Proc. Roy. Soc. A*, 140 (1933), 613.

The integration over all angles of ejection may be carried out analytically; we obtain

$$I_{\kappa}(\theta, \phi) d\omega d\kappa = \frac{2^{10}\kappa k_{\kappa}}{a_0^2 k K^2} \frac{\mu^6 \{K^2 + \frac{1}{3}(\mu^2 + \kappa^2)\}}{\{\mu^4 + 2\mu^2(K^2 + \kappa^2) + (K^2 - \kappa^2)^2\}^3} \times \exp\left\{-\frac{2\mu}{\kappa} \arctan \frac{2\mu\kappa}{K^2 - \kappa^2 + \mu^2}\right\} (1 - e^{-2\pi\mu/\kappa})^{-1} d\omega d\kappa. \quad (22)$$

In Fig. 40 two angular distributions of scattered electrons are illustrated,

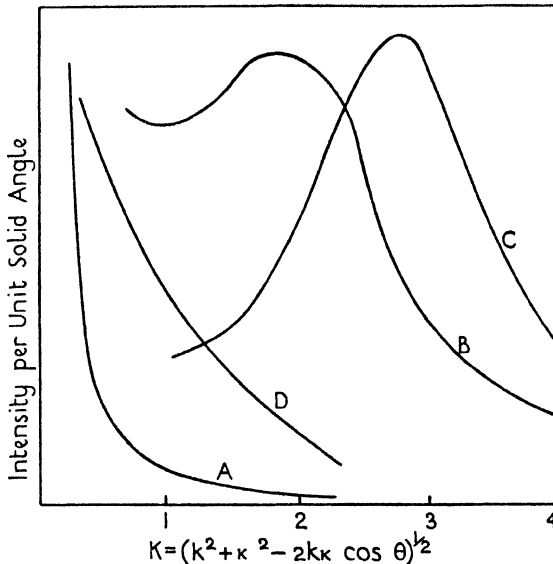


FIG. 41. Angular distribution of electrons scattered after ionizing a helium atom.

<i>Incident electron</i>	<i>Ejected electron</i>
A $k = 4.7$ (300 volts)	$\kappa = 0.5$ (2.5 volts)
B $k = 4.7$ (300 volts)	$\kappa = 2.0$ (55 volts)
C $k = 5.9$ (472 volts)	$\kappa = 3.0$ (122 volts)
D $k = 4.7$ (300 volts)	$\kappa = 1.0$ (14 volts)

calculated from this formula, while in Fig. 41 a number of curves are given in terms of the change of momentum K as variable. From these curves we note:

(a) For small velocities of ejection of the atomic electron the angular distribution of the scattered electron falls off uniformly with angle, just as for the discrete excitations.

(b) For higher velocities of ejection of the atomic electron the angular distribution has a sharp maximum at the point where

$$K^2 = \kappa^2, \quad (23)$$

corresponding to the conservation of momentum in the collision between the atomic and incident electron.

(c) The probability falls off rapidly for large values of K .

2.21. Velocity distribution of ejected electrons

The velocity distribution of the ejected electrons will be obtained by integrating the expression (22) over all angles of scattering. This may

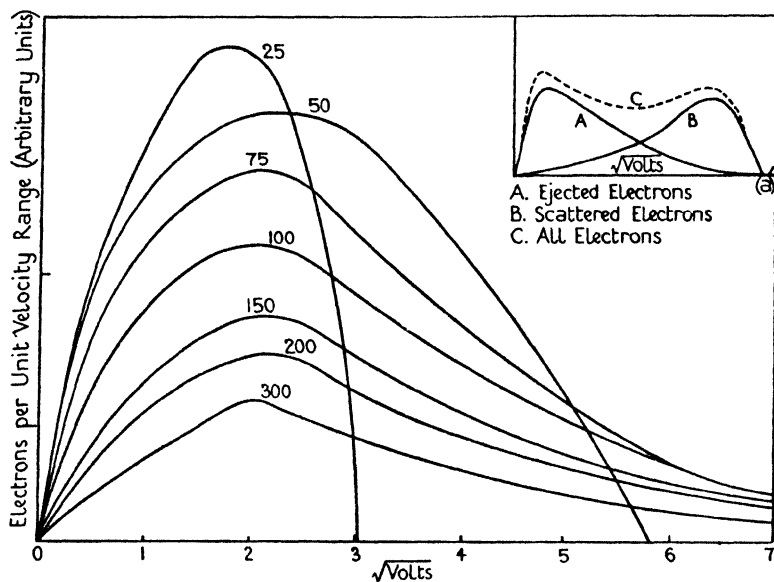


FIG. 42. Velocity distribution of ejected electrons resulting from ionizing collisions with hydrogen atoms.

Numbers denote voltage of incident electrons.

be carried out numerically. In Fig. 42 a number of velocity distributions are illustrated. For ionization by electrons of incident energies greater than 100 volts the probability of ejection rises rapidly to a maximum for low velocities of ejection and falls off quite rapidly with increasing velocity.

As a consequence of the strong asymmetry of the velocity distribution curve for the ejected electrons, we see that interference should only become important for electrons of intermediate velocity. The general form of the resultant distribution is as shown in the inset of Fig. 42 by the dotted line. The observations of Tate and Palmer† provide a qualitative confirmation of this result.

We are now in a position to examine the conditions under which

† *Phys. Rev.* **40** (1932), 731.

interference may be neglected in discussing the angular distributions. From Fig. 42 it appears that the electrons with low energy should have angular distributions comparable with that calculated from (21) for the ejected electrons, while those with high energy should have angular distributions of the form given by (22) for the scattered electrons. Electrons of intermediate velocity should have angular distributions showing marked interference effects. There is little experimental evidence on this subject,[†] but Tate and Palmer (*loc. cit.*) have shown that in mercury vapour the angular distribution of the faster electrons resulting from an ionizing collision (the 'scattered' electrons) is very similar to that of electrons resulting from the excitation of discrete levels, i.e. falling off very rapidly with angle of scattering. This is in agreement with the calculated form of curve illustrated in Fig. 40. For the group of slow electrons they find a comparatively small variation of intensity with angle; this would be expected from the form of the curves in Fig. 40 for the ejected electrons when allowance is made for the fact that in the experiments the collected electrons were not homogeneous, but had a voltage range of 30 volts, which would smooth out any maxima which might have appeared. No definite experimental evidence as to interference effects has yet been obtained.

2.3. *Angular distribution of the aggregate of inelastically scattered electrons*

2.31. *Hydrogen atoms.* Formula (10) gives us the differential cross-section corresponding to a given final state n . If the hydrogen atom is initially in the ground state, we have, summing over all possible states,

$$\sum_{n \neq 0} I_{0n}(K) dK = \frac{128\pi^5 m^2 \epsilon^4}{h^4 k^2 K^3} \sum_{n \neq 0} \left| \int e^{iKx} \psi_0 \psi_n^* d\tau \right|^2 dK. \quad (24)$$

Now, if we expand $e^{iKx}\psi_0$ in a series of atomic wave functions, we obtain

$$e^{iKx}\psi_0 = \sum_n \psi_n \int e^{iKx}\psi_0 \psi_n^* d\tau.$$

Multiplying this equation by its conjugate gives

$$|\psi_0|^2 = \left| \sum_n \psi_n \int e^{iKx}\psi_0 \psi_n^* d\tau \right|^2.$$

Integrating both sides of this equation over all space, we obtain, by virtue of the orthogonal properties of the wave functions ψ_n ,

$$1 = \left| \int e^{iKx} |\psi_0|^2 d\tau \right|^2 + \sum_{n \neq 0} \left| \int e^{iKx} \psi_0 \psi_n^* d\tau \right|^2.$$

[†] For a detailed account see Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chap. III.

Substituting in (24) then gives

$$\sum_{n \neq 0} I_{0n}(K) dK = \frac{128\pi^5 m^2 \epsilon^4}{\hbar^4 k^2} \frac{dK}{K^3} [1 - \{F(K)\}^2], \quad (25)$$

where F is the atomic scattering factor [see Chap. VII, § 1, eq. (9)] for the hydrogen atom, given by

$$\begin{aligned} F(K) &= \int e^{iKx} |\psi_0|^2 d\tau \\ &= (1 + \frac{1}{4} K^2 a_0^2)^{-2}. \end{aligned}$$

The condition of validity of this formula is that no appreciable contribution to the sum (24) arises from transitions $0 \rightarrow n$ which are not energetically possible. For this to be so, K must be greater than the minimum momentum change for a transition to the highest state with appreciable excitation probability; i.e. if E_κ is the energy of this state, we must have, using the expression (13) for K_{\min} ,

$$K > 4\pi^2 m (E_\kappa - E_0) / \hbar k^2.$$

The excitation probability falls off rapidly with increasing E_κ and can certainly be taken as small when

$$E_\kappa > -4E_0.$$

The condition of validity of the formula (25) is then roughly that

$$K > 20\pi^2 m |E_0| / \hbar k^2.$$

If the energy E of the incident electron is great compared with the excitation energy of the state of the atom excited, we have

$$K^2 = (2k^2 - \lambda_n^2)(1 - \cos \theta) + \frac{1}{4} \frac{\lambda_n^4}{k^2} \cos \theta + \dots,$$

where

$$\lambda_n^2 = \frac{8\pi^2 m}{\hbar^2} (E_n - E_0).$$

For all angles θ which satisfy

$$\theta \gg \frac{\lambda_n^2}{k^2}, \quad \text{i.e.} \gg \frac{|E_0|}{E} \quad (26)$$

we have, therefore, $K = 2k \sin \frac{1}{2}\theta$, $k_n \simeq k$. (27)

This result is independent of n and may be used provided $E \gg E_n - E_0$, i.e. for small angle collisions (see Fig. 40). For large angle collisions we make use of the fact that the momentum of the secondary electron ejected is approximately equal to $\hbar K / 2\pi$, so the energy lost by the incident electron is

$$E_\kappa - E_0 = \frac{8\pi^2 m}{\hbar^2} K^2 = \frac{8\pi^2 m}{\hbar^2} (k^2 + k_\kappa^2 - 2kk_\kappa \cos \theta).$$

But
$$E_{\kappa} - E_0 = \frac{8\pi^2 m}{h^2} (k^2 - k_{\kappa}^2),$$

so
$$K = k \sin \theta, \quad k_{\kappa} = k \cos \theta. \tag{28}$$

These formulae are identical with (27) when θ is small, and so we may use (28) for all θ satisfying (26).

As (28) shows that K and k_{κ} are independent of the excitation energy, we may immediately convert the sum (25) for a fixed momentum change to a sum at a fixed angle of scattering by using the relation

$$K dK = k k_n \sin \theta d\theta$$

in connexion with (28). This gives

$$2\pi \sum_n I_{0n}(\theta) \sin \theta d\theta = \frac{128\pi^5 m^2 \epsilon^4}{h^4 k^4} \frac{\cos \theta}{\sin^3 \theta} \left[1 - \frac{1}{(1 + \frac{1}{4} k^2 a_0^2 \sin^2 \theta)^4} \right] d\theta$$

which is to be compared with formula (9) of Chapter IX for the elastic scattering

$$2\pi I(\theta) \sin \theta d\theta = \frac{128\pi^5 m^2 \epsilon^4 a_0^4}{h^4} \frac{(8 + 4k^2 a_0^2 \sin^2 \frac{1}{2} \theta)^2}{(4 + 4k^2 a_0^2 \sin^2 \frac{1}{2} \theta)^4} \sin \theta d\theta.$$

For small angles of scattering [but still satisfying (26)] we have

$$\frac{\sum_n I_{0n}(\theta)}{I(\theta)} = \cot \theta. \tag{29}$$

Hence the inelastic scattering at small angles considerably exceeds the elastic.

At large angles

$$2\pi \sum_n I_{0n}(\theta) = \frac{128\pi^5 m^2 \epsilon^4}{h^4 k^4} \operatorname{cosec}^4 \theta, \tag{30}$$

which is the Rutherford formula for scattering of one electron by another. We must correct this formula to include the interference of the scattered and ejected electrons. Using the formula (26) of Chapter V when ϵ^2/hv is small we obtain

$$\begin{aligned} 2\pi \sum_n I_{0n}(\theta) \sin \theta d\theta &= \frac{128\pi^5 m^2 \epsilon^4}{k^4 h^4} \sin \theta \cos \theta (\operatorname{cosec}^4 \theta - \operatorname{cosec}^2 \theta \sec^2 \theta + \sec^4 \theta) \\ &= \frac{64\pi^5 m^2 \epsilon^4}{k^4 h^4} \frac{4 - 3 \sin^2 2\theta}{\sin^2 2\theta} d\theta. \end{aligned} \tag{31}$$

This is to be compared with the corresponding formula for the elastic scattering

$$2\pi I(\theta) \sin \theta d\theta \sim \frac{16\pi^5 m^2 \epsilon^4}{h^4 k^4} \frac{\cos \frac{1}{2} \theta}{\sin^3 \frac{1}{2} \theta} d\theta. \tag{32}$$

From formulae (29) and (31) we see that inelastic scattering pre-

dominates near 0° and 90° but may become smaller than the elastic at intermediate angles.

2.32. *Generalization for complex atoms.* Morse† has shown that, if θ satisfies (26), the total differential cross-section for all inelastic collisions of fast electrons with an atom of nuclear charge $Z\epsilon$ is given by

$$\sum_n I_{0n}(\theta) = \frac{4\pi^4 m^2 \epsilon^4 Z}{k^4 h^4 \sin^4 \frac{1}{2}\theta} S(k \sin \frac{1}{2}\theta), \tag{33}$$

where

$$S = 1 - ZF^2 + \int |\psi_0(\mathbf{r}_1, \dots, \mathbf{r}_Z)|^2 \sum_{k \neq l}^Z \exp\{2ik \sin \frac{1}{2}\theta (r_l \cos \theta_l - r_k \cos \theta_k)\} d\tau_1 \dots d\tau_Z. \tag{34}$$

$\psi_0(\mathbf{r}_1, \dots, \mathbf{r}_Z)$ is the wave function of the ground state of the atom and F is the atom form factor defined in Chap. VII, § 1. Heisenberg‡ has given a method of calculating S if the Thomas-Fermi statistical atom model is used. He finds that

$$S = 1 - \int_0^{x_0} x^2 \left[\left\{ \frac{\phi(x)}{x} \right\}^{\frac{1}{2}} - \nu \right]^2 \left[\left\{ \frac{\phi(x)}{x} \right\}^{\frac{1}{2}} + \frac{1}{2}\nu \right] dx, \tag{35}$$

where $\nu = \mu/(6\pi Z)^{\frac{1}{2}}$, ϕ , x , and μ are as defined in Chap. IX, § 4.1 and x_0 is given by

$$\left\{ \frac{\phi(x_0)}{x_0} \right\}^{\frac{1}{2}} = \nu. \tag{36}$$

Bewilogua§ has calculated S numerically from the formula (35) and his results are given in Table II.

TABLE II

Differential Cross-sections $I_{in}(\theta)$ for Total Inelastic Scattering of Fast Electrons by Atoms, calculated using the Thomas-Fermi field

ν	$\sqrt{(\text{volts}) \sin \frac{1}{2}\theta / Z^{2/3}}$	S	$4Z^{5/3} I_{in}(\theta)$ in units of a_0^2
0.05	0.278	0.319	9,920
0.1	0.556	0.486	942
0.2	1.112	0.674	81.7
0.3	1.668	0.776	18.6
0.4	2.224	0.839	6.35
0.5	2.781	0.880	2.72
0.6	3.337	0.909	1.36
0.7	3.893	0.929	0.75
0.8	4.449	0.944	0.45
0.9	5.005	0.954	0.28
1.0	5.561	0.963	0.19

At small angles the inelastic scattering considerably exceeds the elastic but falls below it at larger angles.

† *Phys. Zeit.* **33** (1932), 443.

‡ *Ibid.* **32** (1931), 737.

§ *Ibid.*, p. 740.

3. Total collision cross-sections

3.1. Excitation of discrete optical levels

The total cross-section corresponding to the excitation of the n th quantum state of a given atom from the ground state is given by

$$\int_{K_{\min}}^{K_{\max}} I_{0n}(K) dK. \tag{37}$$

The limits of integration have been given in equations (13). In order to evaluate this integral approximately, we observe (cf. Fig. 37 and Table I) that $I_{0n}(K)$ becomes very small for such values of K that

$$K^2 > K_0^2, \tag{38}$$

where

$$K_0^2 = 8\pi^2 m |E_0| / \hbar^2.$$

When this condition is not satisfied we may expand $I_{0n}(K)$ in powers of K . We have, from equation (10),

$$I_{0n}(K) dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 \hbar^4} \frac{dK}{K^3} \left| \int e^{iKx} \psi_0 \psi_n^* d\tau \right|^2.$$

Expanding the exponential, we obtain

$$I_{0n}(K) dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 \hbar^4} \frac{dK}{K^3} \{K^2 |x_{0n}|^2 + \frac{1}{4} K^4 |(x^2)_{0n}|^2 + \dots\}, \tag{39}$$

where $x_{0n}, (x^2)_{0n}, \dots$ are the matrix elements of x, x^2, \dots , so that

$$(x^s)_{0n} = \int x^s \psi_0 \psi_n^* d\tau.$$

The expansion (39) is valid provided the condition (38) is not satisfied. When (38) is satisfied, $I_{0n}(K)$ is very small and may be neglected. We may then write

$$Q_{0n} \simeq \frac{128\pi^5 m^2 \epsilon^4}{k^2 \hbar^4} \int_{K_{\min}}^{K_0} \{K^{-1} |x_{0n}|^2 + \frac{1}{4} K |(x^2)_{0n}|^2 + \dots\} dK.$$

For a transition which is optically allowed the first term will not vanish and will be much the largest for fast electrons. Integrating, since $|E_n|$ is rather less than $|E_0|$ and using the expression (13) for K_{\min} , we obtain

$$Q_{0n} \simeq \frac{64\pi^5 m^2 \epsilon^4}{k^2 \hbar^4} |x_{0n}|^2 \log \frac{2mv^2}{E_n - E_0}. \tag{40}$$

If the transition considered is associated with a quadrupole moment but no dipole moment, we obtain similarly

$$Q_{0n} \simeq \frac{128\pi^7 m^3 \epsilon^4}{k^2 \hbar^6} |(x^2)_{0n}|^2 |E_0|. \tag{41}$$

We notice, then, that owing to the logarithmic term, the cross-sections corresponding to the excitation of optically allowed levels should fall off more slowly with increasing velocity of impact than those corresponding to optically forbidden transitions. Experimental evidence on this point is very meagre. Some evidence is obtained from the measurement of the excitation functions of various spectral lines. This method has been mentioned in Chapter IX. However, the results of the most recent experiments carried out by Lees† and by Thieme‡ in helium do not indicate any noticeable differences in behaviour between *S*, *P*, and *D* levels with regard to variation of excitation probability with velocity at high velocities.

A further consequence of the formula (40) is that, as the velocity of impact increases, a greater proportion of the collisions are inelastic, since the cross-section for elastic scattering decreases as v^{-2} for high velocities [see Chap. IX, (10)]. This effect is clearly shown in Table V of this chapter.

In Table III a number of values of excitation cross-sections for

TABLE III
Cross-sections in units of πa_0^2

<i>Electron energy in volts</i>	<i>State excited</i>									<i>Sum</i>	<i>Observed</i>
	<i>Elastic</i>	<i>2¹S</i>	<i>2¹P</i>	<i>3¹P</i>	<i>3¹D</i>	<i>4¹P</i>	<i>4¹D</i>	<i>4¹F</i>	<i>5¹P</i>		
100	0.375	0.0084	0.107	0.031	0.053	0.012	0.027	0.040	0.0063	0.538	0.67
200	0.205	0.0047	0.069	0.021	0.028	0.009	0.015	0.020	0.0046	0.313	0.31
400	0.107	0.0025	0.047	0.013	0.025	0.006	0.08	0.010	0.0034	0.178	—

helium calculated by use of the exact expression (18) are given with the elastic cross-section for comparison. The observed values given for the sum of the elastic and discrete excitation cross-sections are obtained by subtracting the observed ionization probabilities (compared with those calculated in § 3.3) measured by Smith,§ from the total cross-sections measured by Normand.|| The agreement at 200 volts is very satisfactory, but it appears that Born's approximation begins to fail for electrons with energies less than about 150 volts.

The comparison of relative values for the different transitions with the values obtained from optical experiments is discussed in § 5.2 in connexion with the excitation of triplet levels.

† *Proc. Roy. Soc. A*, **137** (1932), 173.

§ *Phys. Rev.* **36** (1930), 1293.

‡ *Zeits. f. Physik*, **78** (1932), 412.

|| *Ibid.* **35** (1930), 1217.

3.2. *Excitation of X-rays*

In collisions with complex atoms an electron may be ejected from an inner shell, with subsequent X-ray emission. It is thus of considerable interest to obtain approximate expressions for the probability of such inner-shell ionization. We require to sum the probabilities of all the possible transitions from the inner shell concerned.

For ionization of the nl level we require, then,

$$\sum_{n'l'} I_{nl,n'l'}(K) dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 h^4} \frac{dK}{K^3} \sum_{n'l'} \zeta_{nl,n'l'} |\epsilon_{nl,n'l'}(K)|^2. \quad (42)$$

The total cross-section corresponding to this ionization, which we denote by Q_{nl}^i , is then given by

$$Q_{nl}^i = \sum_{n'l'} \int_{K_{\min}}^{K_{\max}} I_{nl,n'l'}(K) dK, \quad (43)$$

and we may approximate to the value of this integral in the same way as in the preceding section for optical levels. In this way we find

$$Q_{nl}^i \simeq \frac{64\pi^5 m^2 \epsilon^4}{k^2 h^4} Z_{nl} (\bar{x}_{nl}^2 - \sum_{n'l'} |x_{nl,n'l'}|^2) \log \left(\frac{2mv^2}{B_{nl}} \right), \quad (44)$$

where B_{nl} is of the order of the energy of ionization of the nl shell and \bar{x}_{nl}^2 is one-third of the mean square radius of the nl shell. For outer shells the terms $\sum_{n'l'} |x_{nl,n'l'}|^2$ are small, and the probability of ionization of the shell is nearly proportional to the mean square radius of the shell, but for inner shells the intensity of forbidden transitions becomes important. Bethe† has carried out further approximations by assuming the atomic wave functions to be of hydrogen-like form with effective nuclear charge Z_{eff} . With this assumption he finds, for those inner shells from which the most important discrete transitions are forbidden,

$$\bar{x}_{nl}^2 - \sum_{n'l'} |x_{nl,n'l'}|^2 = 0.2 - 0.6n^2 a_0^2 / Z_{\text{eff}}^2. \quad (45)$$

As the energy E_{nl} of the nl shell is

$$E_{nl} = -2\pi^2 m \epsilon^4 Z_{\text{eff}}^2 / n^2 h^2,$$

we have finally

$$Q_{nl}^i = \frac{2\pi \epsilon^4 Z_{nl}}{mv^2 |E_{nl}|} b_{nl} \log \left(\frac{2mv^2}{B_{nl}} \right), \quad (46)$$

where b_{nl} is between 0.2 and 0.6 for inner shells, and of the order n^2 for outer shells.

Detailed calculations have been carried out by Burhop‡ for the ionization of the K and L shells of nickel, silver, and mercury by electrons with energies up to 15 times the ionization energy. Born's

† *Ann. der Phys.* 5 (1930), 325.

‡ *Proc. Camb. Phil. Soc.* 36 (1940), 43.

approximation was used throughout with the same effective nuclear charge taken for both the continuous and initial state wave function. If the contribution to Q_{nl}^i due to transitions to unoccupied discrete levels can be neglected, the best values to take for b_{nl} and B_{nl} in (46) may be obtained. It is found then that $b_{nl} \simeq 0.35$ for the K and $\simeq 0.25$ for the L_I , L_{II} , and L_{III} shells and that $B_{nl} = 1.65E_{nl}$ approximately for all four cases.

The formula (46) is only valid for electron energies several times the ionization energy E_{nl} . Burhop's calculations give the results of Born's approximation down to the lowest effective energies. Comparison of his results with the observations of Clark† and of Webster, Hansen, and Duvencok‡ for ionization of the K shell of silver, of Smick and Kirkpatrick§ and of Pockman, Webster, Kirkpatrick, and Haworth|| for the K shell of nickel, and, less definitely, with those of Webster, Pockman, and Kirkpatrick†† for the L shells of gold, reveal the same general discrepancies. The absolute values of the cross-section for electrons with energy ranging from E_{nl} to $3E_{nl}$, at which the cross-section is a maximum, agree very well, but at higher electron energies the observed values fall off less rapidly than the calculated. This is somewhat surprising as it is for these energies that Born's approximation would be expected to be most accurate. It may be that the scale of the observed absolute values is not accurate, so that there really is agreement at high energies and disagreement at smaller where the theoretical values would exceed the observed. This would be consistent with the nature of the failure of Born's approximation when applied to optical excitation (see §§ 3.1, 5) and outer-shell ionization (§ 3.32). On the other hand, the inclusion of relativistic effects will tend to increase the theoretical values at higher energies (see Chap. XV, § 2) and this may be sufficient to remove a large part of the discrepancy.

3.3. Primary ionization

Using the differential cross-sections $I_{0\kappa} d\kappa dK$ given in § 2.2 for the excitation of a level of the continuous spectrum, we may calculate (by numerical integration) the total cross-section Q_0^i for ionization, using the formula

$$Q_0^i = \int_0^{\kappa_{\max}} \int_{K_{\min}}^{K_{\max}} I_{0\kappa}(K) dK d\kappa, \quad (47)$$

where

$$\kappa_{\max}^2 = k^2 - 8\pi^2 m |E_0| / \hbar^2.$$

† *Phys. Rev.* **48** (1935), 30.

‡ *Ibid.* **43** (1933), 851.

§ *Ibid.* **67** (1945), 153.

|| *Ibid.* **71** (1947), 330.

†† *Ibid.* **44** (1933), 130.

The results of such a calculation are illustrated in Figs. 43 and 44 for the ionization cross-sections of hydrogen and helium.

The comparison between experimental curves and those calculated is also shown. The most recent experimental measurements have been carried out by P. Smith and Tate† for (molecular) hydrogen and by P. Smith‡ for helium. For purposes of comparison it is assumed that the molecule behaves like two atoms.

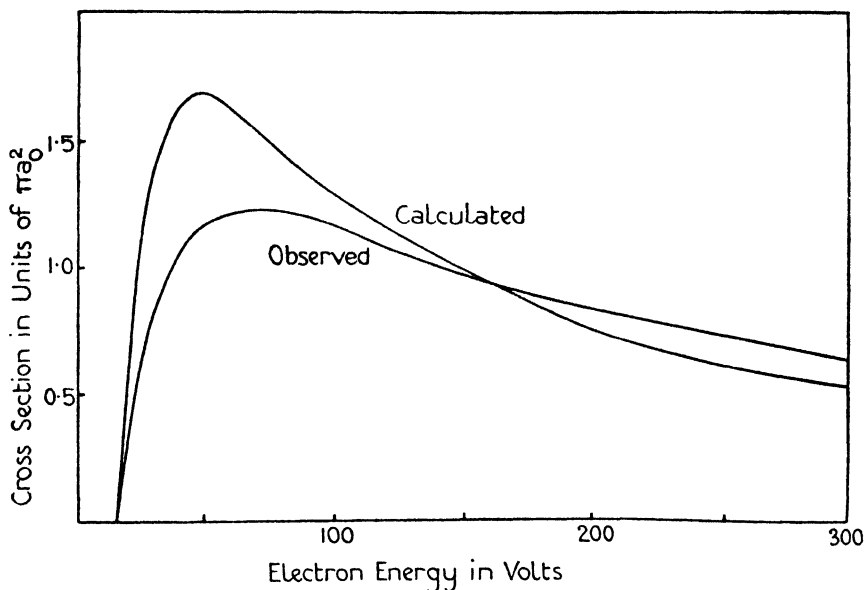


FIG. 43. Ionization probabilities in hydrogen.

The agreement is quite satisfactory when one takes into account the facts that the magnitudes of the cross-sections are compared as well as the variation with velocity, and that it is difficult to obtain approximately correct wave functions to represent ionized states of atoms other than hydrogen. For electrons with energies less than 200 e.V. the theoretical cross-sections are too large, but the disagreement at these low energies of impact is not surprising and will be discussed further in § 5.2. It may be pointed out that the simple theory again predicts too rapid a rise of the probability as the incident energy is increased above the ionization potential, just as for X-ray and optical excitation.

3.31. *Ionization probability for high-velocity impacts.*§ Owing to the

† *Ibid.* **39** (1932), 270.

‡ *Ibid.* **36** (1930), 1293.

§ By high velocity is understood a velocity greater than 1,000 e.V. but not such a velocity that relativistic effects are important.

laborious nature of the calculations for the higher voltage impacts carried out as above, it is important to obtain an approximate formula to cover these cases. In Fig. 42 of this chapter, curves are given which illustrate the dependence of the integral

$$\int_{K_{\min}}^{K_{\max}} I_{0\kappa}(K) dK \quad (48)$$

on κ for various velocities of incidence.

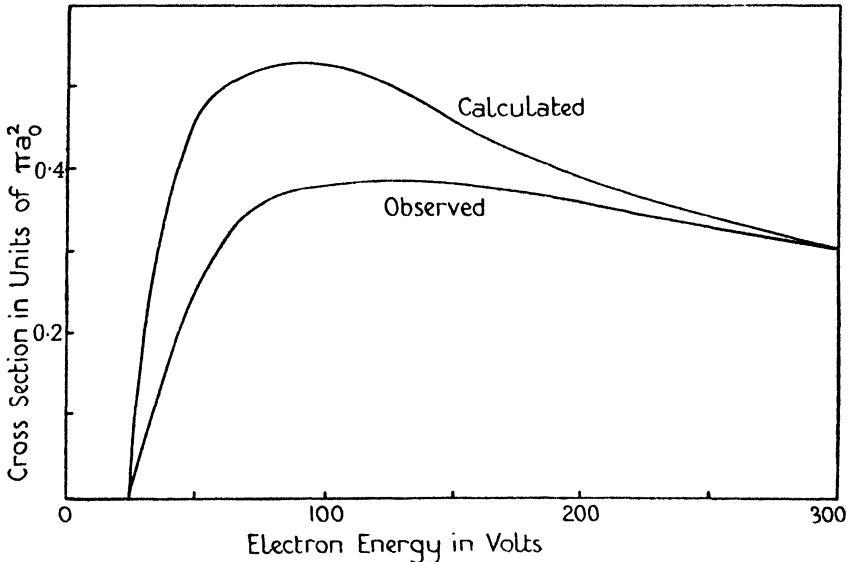


FIG. 44. Ionization probabilities in helium.

Referring to this figure, we see that the main contribution to the probability of ionization comes from transitions involving quite small values of κ . For such transitions $I_{0\kappa}(K)$ is of the form illustrated in Fig. 41; thus for large values of K it is vanishingly small, just as in the case of the excitation of discrete states. The concentration of the scattered electrons about the angle corresponding to the conservation of momentum occurs only for transitions associated with large values of K . As a consequence we may approximate to the value of Q_0^i in much the same way as for the excitation of discrete states. Using this method, we find

$$Q_{nl}^i = \frac{64\pi^5 m^2 \epsilon^4}{h^4 k^2} Z_{nl} \int d\kappa |x_{nl,\kappa}|^2 \log\left(\frac{2mv^2}{C_{nl}}\right), \quad (49)$$

where C_{nl} is a quantity of the order of the energy of the shell. Em-

ploying methods similar to those used in considering the excitation of X-rays it was shown by Bethe† that (49) reduces to

$$Q_{nl}^i = \frac{2\pi\epsilon^4}{mv^2} \frac{c_{nl}}{|E_{nl}|} Z_{nl} \log\left(\frac{2mv^2}{C_{nl}}\right), \tag{50}$$

where

$$c_{nl} = (Z_{\text{eff}}^2/n^2a_0^2) \int |x_{nl,\kappa}|^2 d\kappa.$$

Using again the approximation of hydrogen-like wave functions, the following are the values of c_{nl} for the various shells.

TABLE IV

Shell	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
c_{nl}	0.28	0.21	0.13	0.17	0.14	0.07	0.15	0.13	0.09	0.04

These figures show that shells with the highest azimuthal quantum numbers are the most difficult to ionize.

For hydrogen in particular, for which exact calculation may be carried out,‡ we have for the cross-section for ionization

$$Q_0^i = 0.285 \frac{2\pi\epsilon^4}{|E_0|mv^2} \log\left(\frac{2mv^2}{0.048|E_0|}\right), \tag{51}$$

showing that C_{nl} is about one-tenth of the energy of ionization of the nl shell.

3.32. *Comparison with classical theory and with experiment.* The classical formula of J. J. Thomson§ is of a somewhat different form from (50), as it contains no logarithmic term. The formula is

$$Q_0^i = \frac{2\pi\epsilon^4}{mv^2} \frac{Z_{nl}}{|E_{nl}|}. \tag{52}$$

The very different form of the classical and quantum theoretical expressions makes a comparison with experiment of especial interest. The best substance to choose for the comparison is hydrogen; the use of approximate wave functions is here least likely to lead to serious error, it being unlikely that any important difference between the molecule and atom exists, except the ionization potential which we must take to be that of the molecule (16 volts). The observations of Williams and Terroux|| for $v = 0.54c$ give the number of ions produced per cm. path at N.T.P. as 12.6. The formula (51) gives 14.7, and the classical formula (52) 3.5. The quantum theory formula thus gives much better agreement.

† *Ann. der Phys.* 5 (1930), 325.

‡ Bethe, loc. cit.

§ *Phil. Mag.* 23 (1912), 449.

|| *Proc. Roy. Soc. A*, 126 (1930), 289.

3.4. Distribution of various types of collisions for high-velocity impacts

In Table V† the relative probabilities of different types of collision of high-velocity electrons with hydrogen atoms are given. These values include all relativistic corrections (see Chap. XV, § 2).

TABLE V

Type of collision	Energy of incident electron in volts					
	1,000	10,000	100,000	10 ⁶	10 ⁸	10 ¹⁰
	<i>Percentage of all collisions</i>					
Elastic	8.7	6.5	5.1	4.1	2.55	1.8
Excitation of 2-quantum levels	42.8	45.3	47.5	49.5	51.5	52.8
" " 3- " "	6.3	7.0	7.3	7.8	8.1	8.4
" " 4- " "	2.41	2.60	2.71	2.79	2.90	2.96
" " 5- " "	1.17	1.24	1.28	1.32	1.36	1.38
" " higher " "	2.17	2.28	2.33	2.38	2.42	2.45
All discrete levels	54.8	58.4	61.2	63.4	66.4	68.0
Ionization	36.5	35.1	33.7	32.5	31.0	30.2
Energy-loss per primary ion in volts	51.4	59.9	64.8	66.9	68.6	69.4
" " collision " "	18.7	21.0	21.7	21.7	21.3	21.0
Total cross-section by 10 ⁻²⁰ cm.	3,200	426	66.0	30.6	42.8	60.0

4. Calculation of the stopping-power of matter for fast electrons

4.1. Hydrogen. Preliminary theorems

4.11. *Generalized transition probabilities and oscillator strengths.* It will be found convenient in the calculation of the total energy loss per cm. path of electrons in passing through matter to define certain quantities associated with the various transitions. These quantities are generalizations of quantities associated with optical transitions.

The optical transition probability associated with a transition from the m th to the n th level is defined as

$$\phi_{mn} = 16\pi^4 m^2 \epsilon^4 |x_{mn}|^2 / h^4. \quad (53)$$

We generalize this quantity by writing

$$\phi_{mn}(K) = \frac{16\pi^4 m^2 \epsilon^4}{h^4 K^2} |\epsilon_{mn}(K)|^2,$$

which reduces to (53) for zero momentum change. Associated with the optical transition probability $\phi_{mn}(0)$ is the oscillator strength f_{mn} , which is defined as

$$f_{mn} = R^{-1} \nu_{mn} \phi_{mn},$$

where R is Rydberg's constant and ν_{mn} is the frequency associated with the transition. The generalized oscillator strength associated with the

† Due to Bethe, *Handbuch der Physik*, 2nd edition, xxiv/1 (1933), 519.

$m \rightarrow n$ transition is then defined as†

$$f_{mn}(K) = (E_m - E_n) \frac{8\pi^2 m}{K^2 \hbar^2} |\epsilon_{nm}(K)|^2.$$

We note that the differential cross-section corresponding to the $0 \rightarrow n$ transition is given by

$$I_{0n}(K) dK = \frac{16\pi^3 m \epsilon^4}{k^2 \hbar^2} \frac{1}{E_0 - E_n} f_{0n}(K) \frac{dK}{K}.$$

The loss of energy per cm. path in passing through a gas containing N atoms per c.c. will thus be [cf. equation (59)]

$$-\frac{dT}{dx} = \frac{16\pi^3 m \epsilon^4 N}{k^2 \hbar^2} \sum_n \int_{K_{\min}}^{K_{\max}} f_{0n}(K) \frac{dK}{K}. \quad (54)$$

4.12. *Summation theorem for generalized oscillator strengths.* Let us consider the value of

$$\sum_n f_{0n}(K) = \frac{8\pi^2 m}{K^2 \hbar^2} \sum_n (E_0 - E_n) \left| \int e^{iKx} \psi_0 \psi_n^* d\tau \right|^2.$$

The functions ψ_0, ψ_n^* satisfy the equations

$$\nabla^2 \psi_0 + \frac{8\pi^2 m}{\hbar^2} (E_0 - V) \psi_0 = 0, \quad (55.1)$$

$$\nabla^2 \psi_n^* + \frac{8\pi^2 m}{\hbar^2} (E_n - V) \psi_n^* = 0. \quad (55.2)$$

Multiplying (55.1) by ψ_n^* and (55.2) by ψ_0 , subtracting, and integrating over all space, we obtain

$$(E_0 - E_n) \int e^{iKx} \psi_0 \psi_n^* d\tau = \frac{\hbar^2}{8\pi^2 m} \int (\psi_0 \nabla^2 \psi_n^* - \psi_n^* \nabla^2 \psi_0) e^{iKx} d\tau.$$

The right-hand side reduces to

$$\frac{\hbar^2}{8\pi^2 m} \left\{ -2iK \int \frac{\partial \psi_0}{\partial x} \psi_n^* e^{iKx} d\tau + K^2 \int \psi_0 \psi_n^* e^{iKx} d\tau \right\}. \quad (56)$$

Now

$$\sum_n \left[\int \frac{\partial \psi_0}{\partial x} \psi_n^* e^{iKx} d\tau \right] \left[\int \psi_n \psi_0^* e^{-iKx} d\tau \right] = \int \frac{\partial \psi_0}{\partial x} \psi_0^* d\tau = 0,$$

as may be proved by following a method similar to that used in § 2.3.

† Bethe, *Ann. der Phys.* 5 (1930), 325.

We then have

$$\begin{aligned} \frac{8\pi^2 m}{K^2 \hbar^2} \sum_n (E_0 - E_n) \left| \int e^{iKx} \psi_0 \psi_n^* d\tau \right|^2 &= \sum \left| \int \psi_n \psi_0^* e^{iKx} d\tau \right|^2 \\ &= \left| \int |\psi_0|^2 d\tau \right|^2 = 1. \end{aligned}$$

Hence finally we see that $\sum_n f_{0n}(K) = 1$. (57)

4.2. Calculation of the stopping-power of hydrogen

The loss of energy per cm. path, $-dT/dx$, of an electron passing through a gas containing N atoms per c.c. is given by

$$-\frac{dT}{dx} = N \sum_n \int_{K_{\min}}^{K_{\max}} (E_0 - E_n) I_{0n}(K) dK, \quad (58)$$

which reduces to [cf. eq. (54)]

$$-\frac{dT}{dx} = \frac{16\pi^2 m \epsilon^4 N}{k^2 \hbar^2} \sum_n \int_{K_{\min}}^{K_{\max}} f_{0n}(K) \frac{dK}{K}. \quad (59)$$

We cannot at once use the summation theorem (57) to evaluate the sum, as K_{\min} is a function of n ; we therefore divide the range of integration into two halves, according as K is greater or less than K_0 , where

$$K_0 = \left\{ \frac{8\pi^2 m}{\hbar^2} |E_0| \right\}^{\frac{1}{2}}. \quad (60)$$

At first sight it would not appear to be necessary to take into account momentum changes greater than the quantity (60), since it was shown in previous sections that for such large values of K , $I_{0n}(K)$ is very small; but transitions in which there is a large momentum change are associated with large energy losses and so give appreciable contributions to the sum (59). In fact we shall show below that both ranges give approximately equal contributions to the energy loss. We denote the two contributions to the energy loss per cm. by E' , E'' respectively.

For the calculation of E' , the energy loss in transitions with small change of momentum, we expand e^{iKx} in powers of K as in (39) so

$$E' = \frac{128\pi^5 m^2 N \epsilon^4}{k^2 \hbar^4} \sum_n (E_n - E_0) |x_{0n}|^2 \int_{K_{\min}}^{K_0} \frac{dK}{K}.$$

We may now use the formula

$$\frac{8\pi^2 m}{\hbar^2} \sum_n (E_n - E_0) |x_{0n}|^2 = 1, \quad (61)$$

which gives

$$E' = \frac{16\pi^3 m N \epsilon^4}{k^2 \hbar^2} \left\{ \log K_0 - \frac{8\pi^2 m}{\hbar^2} \sum_n (E_n - E_0) |x_{0n}|^2 \log K_{\min} \right\}. \quad (62)$$

Since we are dealing with fast electrons, we may use the approximate expression derived in § 1.1 for K_{\min} , viz.

$$K_{\min} = 4\pi^2 m (E_n - E_0) / k \hbar^2.$$

Substituting in (62) and remembering that

$$-E_n = 2\pi^2 m \epsilon^4 / \hbar^2 n^2 = R \hbar / n^2, \quad -E_0 = 2\pi^2 m \epsilon^4 / \hbar^2 = R \hbar,$$

we obtain finally

$$E' = \frac{16\pi^3 m N \epsilon^4}{k^2 \hbar^2} \left\{ \log K_0 - \frac{8\pi^2 m R}{\hbar} \sum_n \left(1 - \frac{1}{n^2} \right) |x_{0n}|^2 \log \frac{4\pi^2 m R}{k \hbar} \left(1 - \frac{1}{n^2} \right) \right\}. \quad (63)$$

For the energy loss E'' due to large momentum changes we have

$$E'' = N \sum_n \int_{K_0}^{K_{\max}} (E_n - E_0) I_{0n}(K) dK. \quad (64)$$

Making use of the summation formula (57), we obtain

$$E'' = \frac{16\pi^3 m \epsilon^4 N}{k^2 \hbar^2} \int_{K_0}^{K_{\max}} \frac{dK}{K}. \quad (65)$$

In fixing K_{\max} it is important to note that the expressions given by Born's approximation for $I_{0n}(K)$ are no longer valid if the momentum change is very great. We cannot, therefore, use the expression (13) for K_{\max} in (64), but must employ the condition of conservation of momentum in the collision between the incident and atomic electron. Since the masses of the two electrons are equal, the maximum momentum which the atomic electron can receive will be half the total momentum. We take, then,

$$K_{\max} \simeq k.$$

Carrying out the integration, we obtain

$$E'' = \frac{16\pi^3 m N \epsilon^4}{k^2 \hbar^2} \{ \log k - \log K_0 \}. \quad (66)$$

Adding (66) and (63), we obtain for the total energy loss per cm. path

$$-\frac{dT}{dx} = \frac{4\pi N \epsilon^4}{m v^2} \left\{ \log \frac{m v^2}{R \hbar} - \frac{m^2 \epsilon^4}{\hbar^4} \sum_n |x_{0n}|^2 \left(1 - \frac{1}{n^2} \right) \log \frac{n^2 - 1}{n^2} \right\}. \quad (67)$$

The summation may be carried out numerically using the usual formulae for the matrix elements x_{0n} . The final result is

$$-\frac{dT}{dx} = \frac{4\pi\epsilon^4 N}{mv^2} \log \frac{mv^2}{cR\hbar} \quad (c = 1.105). \quad (68)$$

4.3. Complex atoms

It is possible to generalize the formula (68) for complex atoms if hydrogen-like wave functions are assumed and allowance made for transitions excluded by the upper states concerned being already occupied. This has been done by Bethe,† but the results are not accurate enough for most purposes. Instead it is best to represent the stopping-power of atoms with Z electrons by the formula

$$-\frac{dT}{dx} = \frac{4\pi\epsilon^4 N}{mv^2} Z \log \left(\frac{mv^2}{I} \right), \quad (69)$$

where I is a mean excitation energy. The determination of I is best carried out by experiment, though Bloch‡ has shown how an approximate value may be obtained for it by treating the atom according to the Fermi-Thomas statistical theory.

4.4. Relation to Bohr's classical formula—the method of impact parameters

The classical theory of stopping-power was worked out by Bohr§ in 1913. It differs from the formula (68) in that the argument of the logarithm is multiplied by a quantity of order $h\nu/\epsilon^2$. The range of validity of the different approximations has been discussed by Bloch|| and by Williams.†† We shall follow the method used by the latter author as it gives considerable insight into the relative importance of the phenomena involved.

Consider a fast electron passing through matter containing N atoms per c.c. each of which contains Z electrons. If these electrons were free, the number of collisions per cm. in which the incident electron would be deviated through an angle between θ and $\theta + d\theta$ would be given by the Coulomb scattering formula

$$NZI(\theta) d\theta = (2\pi NZ\epsilon^4/m^2v^4) d\theta/\theta^3,$$

provided θ is not too large. In such a deflexion the energy transfer is

† *Ann. der Phys.* 5 (1930), 325.

‡ *Zeits. f. Physik*, 81 (1933), 363.

§ *Phil. Mag.* 25 (1913), 10; 30 (1915), 58.

|| *Ann. der Phys.* 16 (1933), 285.

†† *Proc. Roy. Soc. A*, 139 (1933), 163; *Rev. Mod. Phys.* 17 (1945), 217.

approximately $mv^2\theta^2$, so the energy loss per cm. caused by collisions in which θ is $> \theta_{\min}$ would be

$$-\frac{dT}{dx} = \frac{2\pi NZ\epsilon^4}{mv^2} \int_{\theta_{\min}}^{\theta_{\max}} \frac{d\theta}{\theta} = \frac{2\pi NZ\epsilon^4}{mv^2} \log\left(\frac{\theta_{\max}}{\theta_{\min}}\right). \quad (70)$$

θ_{\max} can be taken as unity for our purposes as we only wish to obtain the order of magnitude of the argument of the logarithm. On the other hand, the effect of the binding forces may be regarded as providing the lower limit θ_{\min} to insert in (70).

According to classical ideas the binding will only be effective in limiting the energy transfer when the time of collision is comparable with, or greater than, the period of revolution of an electron in its orbit. The time of collision is roughly given by p/v , where p is the impact parameter, measured relative to the atomic nucleus as centre. As the time of revolution in the orbit is of the order h/E , where E is the binding energy, the classical condition for ignoring binding effects is that the impact parameter p should be $< \rho$, where

$$\rho \sim hv/E. \quad (71)$$

If ρ is $\gg d$, where d is of the order of the orbital radius of the atomic electrons, this classical condition will remain valid in quantum theory. For, in these distant collisions, the incident electron is only slightly deviated and its perturbing influence on the atom is capable of classical description.

Since h/E is of the order d/u where u is the orbital velocity of the atomic electrons, the condition $\rho \gg d$ is satisfied if $v^2/u^2 \gg 1$. When this is so it remains only to relate the maximum effective impact parameter ρ to θ_{\min} . This may be done by the same procedure as that described in Chap. VII, § 5, and applied in Chap. IX, § 6, to multiple scattering. We have

$$\begin{aligned} \theta_{\min} &\simeq \frac{\hbar}{mv\rho} & (\epsilon^2/\hbar v \ll 1), \\ &\simeq \frac{\epsilon^2}{mv^2\rho} & (\epsilon^2/\hbar v \gg 1). \end{aligned}$$

Substituting in (70) and using (71) we find

$$-\frac{dT}{dx} = \frac{2\pi NZ\epsilon^4}{mv^2} \log\left(g_1 \frac{mv^2}{E}\right) \quad (\epsilon^2/\hbar v \ll 1), \quad (72)$$

$$= \frac{2\pi NZ\epsilon^4}{mv^2} \log\left(g_2 \frac{mv^3\hbar}{\epsilon^2 E}\right) \quad (\epsilon^2/\hbar v \gg 1), \quad (73)$$

where g_1 and g_2 are quantities of order unity.

Of these expressions (72) is equivalent to the formula (69) while the second is Bohr's classical formula. Thus the condition $u^2/v^2 \ll 1$ is assumed in the derivation of both. For the stopping of electrons this is incompatible with the condition $\epsilon^2/\hbar v \gg 1$, so that the classical formula is never valid for such cases. In Chap. XII, § 2.3, the stopping-power of matter towards heavy particles is considered, and it will be shown there that Bohr's formula is valid over a certain energy range when the particle possesses a large charge.

The above conclusions have been confirmed by a detailed analysis due to Bloch,† while Mott‡ has given a strict proof of the equivalence of the method of impact parameters and Born's approximation under the conditions stated above.

4.5. Comparison with experimental values

The application of the formulae (68) and (70) for the energy loss per cm. of fast electrons in (atomic) hydrogen and other gases has been considered exhaustively by Williams.§ In order to compare the theoretical and experimental values it is necessary to increase the results by about 10 per cent. to allow for the fact that in practice the electron which emerges with the greater energy after the collision is taken as the β -particle. After applying this correction a very good agreement is obtained with experiment, as illustrated in Table VI. The values given

TABLE VI
Range of Fast Electrons in Hydrogen

v/c	u^2/v^2	$\epsilon^2/(\hbar v)$	Range (cm.)		
			Observed	Bethe (Quantal)	Bohr (Classical)
0.17	0.0007	0.06	0.76	0.77	0.52
0.136	0.001	0.07	0.37	0.34	0.23

by Bohr's classical theory are also included. Values of $\epsilon^2/\hbar v$ and u^2/v^2 (where u is the orbital velocity of the atomic electrons) are given. If Bethe's formula (68) is valid both these quantities should be small compared with unity, as indeed they are.

Further evidence in support of the quantum theory of the stopping-power of matter for fast charged particles will be discussed in Chapter XIII in connexion with the passage of heavy particles through matter.

† Loc. cit.

‡ *Proc. Camb. Phil. Soc.* **27** (1931), 553; and Frame, *ibid.* **27** (1931), 511.

§ *Proc. Roy. Soc. A*, **135** (1932), 108.

4.6. Relative contribution of light and heavy collisions to stopping-power

It was shown in § 3.31 that the number s_0 of primary ions produced per cm. path is given by

$$s_0 = \frac{2\pi N \epsilon^4}{mv^2} \sum_{nl} \frac{c_{nl} Z_{nl}}{(-E_{nl})} \log \frac{2mv^2}{C_{nl}},$$

where the quantities c_{nl} , C_{nl} are as defined in equations (49) and (50). The energy loss per primary ion produced is then given by $-\frac{dT/dx}{s_0}$.

For nitrogen this gives, for electrons of 30,000 volts energy, an energy loss per primary ion produced, of roughly 80 volts, and for hydrogen 100 volts. This high value arises from the fact that a larger percentage of collisions lead to excitation than to ionization. The contribution to the energy loss per cm. due to heavy collisions (in which a fast† electron is emitted) is, moreover, quite considerable, owing to the great energy loss in the collision. It is given by

$$\begin{aligned} E'' &= \frac{16\pi^3 m N \epsilon^4}{k^2 h^2} \sum_{nl} Z_{nl} \int_{k_0}^k \frac{dK}{K} \\ &= \frac{8\pi^3 m N \epsilon^4}{k^2 h^2} \sum_{nl} Z_{nl} \log \left(\frac{k^2}{k_0^2} \right), \end{aligned}$$

where $k_0^2 \simeq 8\pi^2 m |E_{nl}| / h^2$. Referring to the expression (68) for $-dT/dx$, we see that heavy collisions account for roughly half the total energy loss.

It is also of interest to note that Williams has used the method of impact parameters to determine the relative importance of close and distant collisions. He finds that for a 100,000 volt electron traversing hydrogen, out of every fourteen atoms ionized or excited, only one lies in the direct path of the electron, and that four lie between 2.5×10^{-7} and 10^{-6} cm.

5. Inelastic collisions of slow electrons with atoms

The theoretical investigation of inelastic collisions of slow electrons is much more complicated than for fast particles. Experimental evidence shows clearly that electron exchange becomes important, and the observations of Mohr and Nicoll‡ of the angular distribution of inelastically scattered electrons in mercury vapour and in argon show that the distortion of the incoming and outgoing waves by the fields

† With energy great compared with the ionization potential.

‡ *Proc. Roy. Soc. A*, **138** (1932), 229 and 469.

of the normal and excited atoms respectively must be taken into account (see below, § 5.3).

It was pointed out at the beginning of this chapter that according to Born's approximation the probability of excitation of a level belonging to a term system different from that of the initial state is zero. For impacts of sufficiently high velocity this is in agreement with observation, but for low-velocity collisions the excitation of these levels takes place quite readily, and at certain velocities may occur even more often

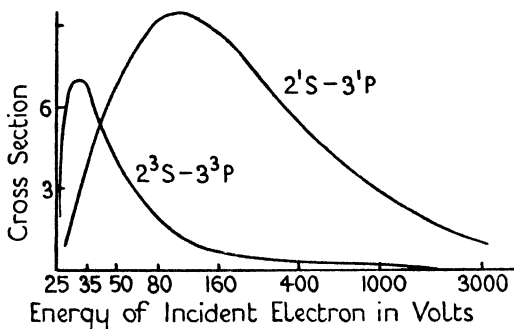


FIG. 45. Observed excitation functions of 3^1P and 3^3P levels in helium. The curves were obtained by measurement of the variation of the intensity of excitation of the spectral lines produced by optical transitions to the 2^1S , 2^3S levels respectively.

than the excitation of a level of the same term series as the initial state. Thus in Fig. 45 we show the excitation probability velocity curves for the excitation of the 3^1P and 3^3P levels of helium from the ground 1^1S state, measured by Lees† using optical methods (see Chap. IX, § 1). When the energy of the exciting electrons is greater than 100 volts, triplet excitation occurs very seldom compared with singlet excitation; but at voltages just above the excitation potential the reverse may be the case. This is a general feature of the observations of the excitation of various two-electron systems.‡ In all cases the triplet excitation curve rises to a maximum very rapidly at about a volt above the excitation potential, whereas the corresponding singlet curve attains a maximum much more gradually (except for S states). The magnitudes of the corresponding maxima are comparable in all cases.

If the coupling between spin and orbital motion is small, triplet excitation can only take place if electron exchange occurs on impact

† *Proc. Roy. Soc.* **137** (1932), 173.

‡ Hughes and Lowe, *ibid.* **A**, **104** (1923), 480; Skinner and Lees, *Nature*, **123** (1929), 836, and Lees, *Proc. Roy. Soc. A*, **137** (1932), 173; Hanle, *Zeits. f. Physik*, **56** (1929), 94; Michels, *Phys. Rev.* **36** (1930), 1362; Thieme, *Zeits. f. Physik*, **78** (1932), 412. For a detailed description of experimental methods and results see Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chap. II.

in such a way as to change the symmetry of the spin function of the atomic electrons. Therefore the experimental results show that the exchange process is important for low-velocity collisions. This process is not limited to excitation of levels of another term system, and must also be taken into account in singlet excitation.

Interesting results have been obtained by Mohr and Nicoll (*loc. cit.*), who investigated the angular distributions of electrons with initial energies between 50 and 120 volts scattered in various gases after

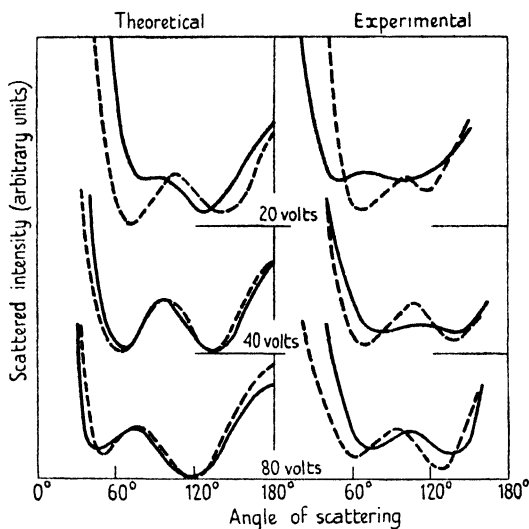


FIG. 46. Calculated and observed angular distributions of electrons scattered by argon atoms.

- Elastically scattered electrons.
- Electrons which have excited the argon resonance level.

exciting the most probable level. Some of the observed curves are illustrated in Fig. 46. For the heavier gases the maxima and minima are very noticeable. The similarity of the diffraction effects observed in angular distributions of elastically and inelastically scattered electrons of the same incident velocity indicates that the two effects are due to the same cause, the distortion of the electron waves by the atomic field. This will be discussed further in § 5.3.

5.1. *Application of theory of collisions*

A completely satisfactory method of dealing with slow inelastic electron collisions does not yet exist, but by using the general theory of Chapter VIII we may obtain approximate formulae for the probabilities

involved. The scattering of electrons which have excited the n th state of atoms of hydrogen and helium may be described by means of two wave functions $F_n(\mathbf{r}_1)$, $G_n(\mathbf{r}_2)$ which have the asymptotic forms

$$\begin{aligned} F_n(\mathbf{r}_1) &\sim f_n(\theta_1, \phi_1) r_1^{-1} \exp(ik_n r_1), \\ G_n(\mathbf{r}_2) &\sim g_n(\theta_2, \phi_2) r_2^{-1} \exp(ik_n r_2). \end{aligned} \quad (74)$$

The differential cross-section for excitation of the n th state is then given by

$$\begin{aligned} I_n(\theta) &= \frac{1}{4} \frac{k_n}{k} \{3|f_n(\theta, \phi) + g_n(\theta, \phi)|^2 + |f_n(\theta, \phi) - g_n(\theta, \phi)|^2\}, \quad \text{for hydrogen,} \\ &= \frac{k_n}{k} |f_n(\theta, \phi) - g_n(\theta, \phi)|^2, \quad \text{for helium.} \end{aligned} \quad (75)$$

In Chapter VIII, equations (38) and (39), these functions are shown to satisfy the equations

$$\begin{aligned} [\nabla_1^2 + k_n^2] F_n(\mathbf{r}_1) &= -\frac{8\pi^2 m \epsilon^2}{\hbar^2} \int \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) \psi_n^*(\mathbf{r}_2) d\tau_2, \\ [\nabla_2^2 + k_n^2] G_n(\mathbf{r}_2) &= -\frac{8\pi^2 m \epsilon^2}{\hbar^2} \int \left(\frac{1}{r_2} - \frac{1}{r_{12}} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2) \psi_n^*(\mathbf{r}_1) d\tau_1. \end{aligned} \quad (76)$$

The function Ψ is the solution of the wave equation for the complete system of atom and incident electron. To solve these equations we must, as in Chap. X, § 6, substitute some approximate form for Ψ on the right-hand side of (76). We shall set on the right-hand side,

$$\Psi = F_0(\mathbf{r}_1) \psi_0(\mathbf{r}_2) + F_n(\mathbf{r}_1) \psi_n(\mathbf{r}_2) + G_n(\mathbf{r}_2) \psi_n(\mathbf{r}_1). \quad (77)$$

Here $F_0(r)$ is the solution representing an incident wave and a scattered wave, as discussed in Chapter II, of

$$\left(\nabla^2 + k^2 - \frac{8\pi^2 m}{\hbar^2} V_{00} \right) F_0 = 0. \quad (78)$$

We note that (77) is not the same approximation as that used in Chap. X, § 6, in dealing with the elastic collisions. By including terms in ψ_n , we ensure that on the right-hand side of (76) all diagonal elements V_{ss} of the interaction energy shall be included. The only non-diagonal matrix elements are those, V_{0n} , which refer to the initial state of the atom.

On substitution in (76) we obtain, by following a similar procedure

to that used in the consideration of the elastic exchange, the equation

$$\begin{aligned} & \left[\nabla_1^2 + k_n^2 - \frac{8\pi^2 m}{\hbar^2} V_{nn}(r_1) \right] \{F_n(\mathbf{r}_1) \pm G_n(\mathbf{r}_1)\} \\ &= -\frac{8\pi^2 m \epsilon^2}{\hbar^2} \left\{ \int \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) [F_0(\mathbf{r}_1) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) \pm F_0(\mathbf{r}_2) \psi_0(\mathbf{r}_1) \psi_n^*(\mathbf{r}_2) + \right. \\ & \quad \left. + \{G_n(\mathbf{r}_2) \pm F_n(\mathbf{r}_2)\} \psi_n(\mathbf{r}_1) \psi_n^*(\mathbf{r}_2)] d\tau_2 \right\}. \quad (79) \end{aligned}$$

The third term on the right-hand side makes further approximation difficult except for high velocities of impact. In this case we may neglect the effect of the atomic field in the zero-order approximation, and write on the right-hand side of (79)

$$F_0(\mathbf{r}_1) = \exp(ik\mathbf{n}_0 \cdot \mathbf{r}_1), \quad G_n(\mathbf{r}_2) = 0.$$

We then obtain

$$\begin{aligned} (\nabla^2 + k_n^2) \{F_n(\mathbf{r}_1) \pm G_n(\mathbf{r}_1)\} &= -\frac{8\pi^2 m \epsilon^2}{\hbar^2} \int \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) \times \\ & \times \{ \exp(ik\mathbf{n}_0 \cdot \mathbf{r}_1) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) \pm \exp(ik\mathbf{n}_0 \cdot \mathbf{r}_2) \psi_0(\mathbf{r}_1) \psi_n^*(\mathbf{r}_2) \} d\tau_2. \quad (80) \end{aligned}$$

Solving this equation by the method of Chap. VI, § 4, we have

$$\begin{aligned} f_n(\theta, \phi) \pm g_n(\theta, \phi) &= \frac{2\pi m \epsilon^2}{\hbar^2} \iint \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) [\exp\{i(k\mathbf{n}_0 - k_n \mathbf{n}_1) \cdot \mathbf{r}_1\} \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) \pm \\ & \quad \pm \exp\{i(k\mathbf{n}_0 \cdot \mathbf{r}_2 - k_n \mathbf{n}_1 \cdot \mathbf{r}_1)\} \psi_0(\mathbf{r}_1) \psi_n^*(\mathbf{r}_2)] d\tau_1 d\tau_2. \quad (81) \end{aligned}$$

A possibly less drastic approximation is to ignore the third term in (79). This term represents the effect of exchange in determining the form of the wave $F_n \pm G_n$. As, in failing to include $G_0(\mathbf{r}_2) \psi_0(\mathbf{r}_1)$ in the approximation (77) we have ignored the similar effect on F_0 , we should omit the term for the sake of consistency. This gives

$$\begin{aligned} f_n(\theta, \phi) - g_n(\theta, \phi) &= \frac{2\pi m \epsilon^2}{\hbar^2} \iint \left(\frac{1}{r_1} - \frac{1}{r_{12}} \right) [F_0(r_1, \theta_1) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) \mathfrak{F}_n(r_1, \pi - \Theta_1) - \\ & \quad - \mathfrak{F}_n(r_1, \pi - \Theta_1) F_0(r_2, \theta_2) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_1)] d\tau_1 d\tau_2, \quad (82) \end{aligned}$$

where $\mathfrak{F}_n(r, \theta)$ is the solution of the homogeneous equation

$$\left[\nabla^2 + k_n^2 - \frac{8\pi^2 m}{\hbar^2} V_{nn}(r) \right] \mathfrak{F}_n(r, \theta) = 0,$$

which has the asymptotic form

$$\mathfrak{F}_n(r, \theta) \sim \exp ik_n z + r^{-1} \exp ik_n r \times \text{function of } \theta, \phi,$$

and $\cos \Theta_1 = \cos \theta \cos \theta_1 + \sin \theta \sin \theta_1 \cos(\phi - \phi_1).$

The interpretation of the formulae (81) and (82) is interesting. The first term represents the directly scattered waves, the second the electron exchange. They are both of the form expected, being the integrals of the interaction energy over the initial and final wave functions of the system. The formula (82) differs from (81) in that the former includes the effect of the potential field V_{nn} on the outgoing wave and of the field V_{00} on the incident wave.

A further approximation might be made by replacing the function F_0 in (82) by $F_0 - G_0$, which satisfies the integro-differential equation (12) of Chapter X, and \mathfrak{F}_n by the solution of the corresponding integro-differential equation when the atom is in its n th excited state.

As far as these approximations are concerned we note that there is a similar difficulty to that discussed in Chap. X, § 5. The form (77) assumed for the function Ψ does not satisfy the orthogonality conditions

$$\begin{aligned} \int \{\Psi - F_n(r_1)\psi_n(r_2)\}\psi_n^*(r_2) d\tau_2 &= 0, \\ \int \{\Psi - G_n(r_2)\psi_n(r_1)\}\psi_n^*(r_1) d\tau_1 &= 0. \end{aligned} \tag{83}$$

For sufficiently high velocities of impact the errors made will be small, but this may not be so for electrons with energies near that of excitation. Furthermore, we have assumed all non-diagonal matrix elements to be small, neglecting the effect of the reaction of the waves F_n , G_n on the incident and elastically scattered wave F_0 . This corresponds to weak coupling between the two sets of waves, but actually, in certain cases, it may be necessary to assume 'close coupling' corresponding to a large value of the non-diagonal matrix element V_{0n} . It will be shown below that the experimental evidence does indicate the necessity for including such effects.

The approximation of neglecting all non-diagonal matrix elements except V_{0n} also fails to include the reaction of the other inelastically scattered waves on the $0-n$ excitation. These last approximations differ from those made above, as they are not introduced by exchange considerations but are inherent in the method of distorted waves (Chap. VIII, § 5) and have already been discussed in that connexion.

5.2. Calculations for helium and comparison with experiment†

The singlet and triplet excitation cross-sections for helium have been calculated as functions of the velocity of the exciting electron,‡ using the approximate formula (81), for several excited states.

† For a more detailed discussion see Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chap. III.

‡ Massey and Mohr, *Proc. Roy. Soc. A*, **132** (1931), 605; *ibid.* **140** (1933), 613.

A number of general features of the experimental results are reproduced. From formula (81) it may be shown that the triplet excitation probability falls off as v^{-4} , v^{-6} , v^{-8} for S , P , D states respectively, in sharp contrast to the variation as v^{-2} , $v^{-2} \log \alpha v$, v^{-2} for the corresponding singlet state, v being the incident electron's velocity.

In the case of both 1S and 3S states detailed agreement is obtained between theory and experiment down to quite low velocities of impact,

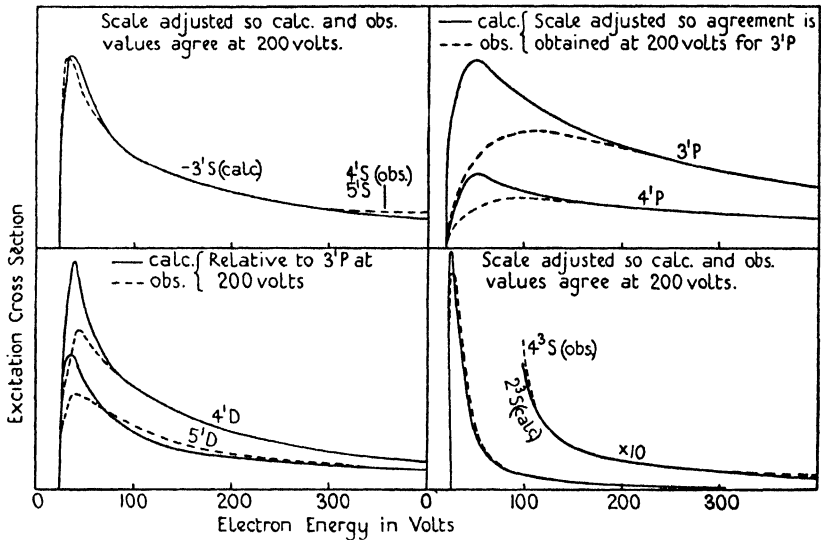


FIG. 47. Comparison of observed and calculated excitation cross-section velocity curves.

but for 1P and 1D states the agreement becomes unsatisfactory for electrons of energy less than 100 and 75 volts respectively. This is illustrated in Fig. 47. Referring to this figure we see that as the electron energy is reduced below 100 volts the calculated probabilities of excitation of the P -levels become considerably greater than the observed. This effect is only apparent for 1D levels at lower velocities and for S states it is doubtful if there is any great discrepancy at any velocity. We showed in §§ 3.2 and 3.3 of this chapter that the same behaviour is a feature of the ionization and X-ray excitation probabilities, and it seems that Born's formula is least valid for the calculation of transition probabilities involving optically allowed transitions. Examining the approximations we have introduced, we see that this almost certainly implies that the failure of the theory in such cases is due to the assumption that V_{0n} is small. Actually, for the excitation of optically allowed levels V_{0n} vanishes only as r^{-2} for large r , and such a field has

a large scattering power (thus the elastic cross-section for such a field is infinite, cf. Chap. II, § 3). To improve the theory it would be necessary to solve simultaneous equations of the same form as those discussed in Chap. VIII, § 6. It was shown there (cf. Chap. VIII, Fig. 18) that accurate solution of these equations will lead to a smaller probability of excitation than that given by Born's approximation, just as is required from the above experimental results. For D levels V_{0n} vanishes as r^{-4} for large r , and this field will have a much smaller scattering power than that corresponding to P excitation. We should thus expect Born's approximation to agree with experiment down to much lower velocities for D excitation, while for S excitation, for which V_{0n} vanishes as $e^{-\lambda r}$ for large r , we expect very little deviation from the simple theory. This, again, is in agreement with the observed results.

The calculated relative magnitudes of triplet and singlet excitation probabilities for electrons of energy greater than 100 volts are in rough agreement with experiment, but it appears that the observed excitation curves for 3P levels fall off much more slowly with velocity than the calculated curves. The reason for this discrepancy is not clear but is probably due to secondary processes occurring in the experimental apparatus.

The excitation of the 2^1P and 2^3P levels has also been considered by the same authors† using formula (82). The wave function \mathfrak{F}_n was calculated numerically by Macdougall‡ and the integration of (82) carried out by numerical methods. The chief interest of this calculation is that it includes the distortion of the incident and outgoing waves by the atom and should include the diffraction effects to be expected. For 50 volt electrons an angular distribution is predicted which is of the form observed by Mohr and Nicoll (loc. cit.), becoming approximately uniform for large angles of scattering but with a faint maximum at 90° . There was no improvement found, however, in the agreement of observed and calculated total cross-sections.

5.3. *Excitation of heavy atoms*

Calculations for the excitation of the $2P$ levels of mercury have been carried out by Penney,§ who also used the formula (81). The chief interest of his calculations is his use of atomic wave functions which include terms arising from the interaction of spin and orbital motion. These are quite appreciable for such a heavy atom as mercury.

† *Proc. Roy. Soc. A*, **139** (1932), 187.

‡ *Proc. Camb. Phil. Soc.* **28** (1932), 341.

§ *Phys. Rev.* **39** (1932), 467.

As a consequence the wave functions for the triplet state 2^3P_1 are not completely antisymmetrical in the orbital wave functions, and so this state can be excited without electron exchange. The excitation of this triplet level therefore persists at high velocities. The calculated ratio of the intensities of the various levels agrees well with experiment even at exciting energies as low as 10 volts. The form of the excitation-velocity curves for all the levels also agrees qualitatively with the observations.

We now consider the diffraction effects observed by Mohr and Nicoll† in electrons scattered inelastically by atoms. If we neglect exchange effects (which is legitimate at moderate to high velocities of impact), the intensity of scattering of electrons which have excited the n th state of a given atom is given per unit solid angle by

$$I_n(\theta) = \frac{k_n}{k} \frac{4\pi^2 m^2}{h^4} \left| \int V_{0n}(\mathbf{r}') F_0(r', \theta') \mathfrak{F}_n(r', \pi - \Theta) d\tau' \right|^2, \quad (84)$$

where
$$V_{0n}(\mathbf{r}) = \int V(\mathbf{r}, \mathbf{r}_a) \psi_0(\mathbf{r}_a) \psi_n^*(\mathbf{r}_a) d\tau_a,$$

the suffix a distinguishing the coordinates of the atomic electrons. The functions $F_0(r, \theta)$, $\mathfrak{F}_n(r, \Theta)$ can be written in the form

$$F_0(r, \theta) = e^{ikr \cos \theta} + \sum_s \left[F_0^s - \sqrt{\left(\frac{2\pi}{kr}\right)} J_{s+\frac{1}{2}}(kr) \right] (2s+1) i^s P_s(\cos \theta), \quad (85)$$

$$\mathfrak{F}_n(r, \pi - \Theta) = e^{-ik_n r \cos \Theta} + \sum_s \left[\mathfrak{F}_n^s - \sqrt{\left(\frac{2\pi}{k_n r}\right)} J_{s+\frac{1}{2}}(k_n r) \right] (2s+1) i^{-s} P_s(\cos \Theta), \quad (86)$$

where the first term denotes a plane wave undisturbed by the atomic field and the series represents the disturbance of the plane waves by the fields of the normal and excited atoms. Substituting in (84), we find that

$$I_n(\theta) = \frac{k_n}{k} \frac{4\pi^2 m^2}{h^4} \left| \int V_{0n} \exp\{i(kr' \cos \theta' - k_n r' \cos \Theta)\} d\tau' + \sum_s P_s(\cos \theta) \int V_{0n} H_s(r', \theta', \phi') d\tau' \right|^2, \quad (87)$$

where H_s is a certain function of r', θ', ϕ' . The first term in the integral is just that given by Born's formula and its behaviour has been discussed in § 2 of this chapter. At angles of scattering greater than 30° it is negligibly small and so the main contribution comes from the series. The number of harmonics which are important in this series determines the diffraction effects at angles greater than 30° . Now, if the energy

† Cf. Fig. 46.

of the incident electron is great compared with the excitation energy, $k_n \simeq k$, and also the fields of the normal and excited atoms will be effectively the same. In this case the same number of terms in the series (85) and (86) will be required, and these will be of the same relative importance as for the elastic scattering, which is described by $F_0(r, \theta)$. The diffraction effects at large angles will therefore be very similar to those occurring in the elastic scattering. This is the observed result.

For low velocities this similarity will disappear, as the field V_{nn} has a much greater spread than V_{00} , and so will affect more harmonics of \mathfrak{F}_n than V_{00} will of F_0 . The difference between k_n and k will also be important at these velocities. This result is a feature of the observations in argon. (Cf. Fig. 46, in which it will be seen that the angular distributions for the inelastically scattered electrons resemble those for the elastically scattered at voltages above 55 volts but become more and more dissimilar as the voltage decreases below this.)

Detailed calculations, using (84), have been carried out by Massey and Mohr,† for the scattering of electrons after exciting the resonance levels of neon and of argon respectively. The general conclusions outlined above were confirmed. Fig. 46 illustrates the comparison between the shape of calculated and observed elastic and inelastic angular distributions for argon.

6. Summary

We show above that, for inelastic collisions of slow electrons with atoms, Born's approximation fails in three ways. It predicts too great a value for the inelastic cross-section and fails to account for the maxima and minima in the inelastic angular distributions. Apart also from its failure to predict the diffraction maxima and minima observed in the elastic scattering of slow electrons by atoms, it also fails to predict the large scattering at small angles, which we have interpreted as due to polarization effects arising from the interaction of inelastic and elastically scattered waves. The whole position is summarized in Table VII.

A physical picture of the way in which the deviations from Born's approximation arise has been given by Massey and Mohr.‡ While the approximation is valid, we may regard an electron as spending such a short time in the atomic field that it undergoes one scattering process at most. As the electron energy is reduced, the chance of the electron

† *Proc. Roy. Soc. A*, **146** (1934), 880.

‡ *Ibid. A*, **140** (1933), 613.

TABLE VII

Analysis of Effects contributing to Scattering Electrons by Atoms

<i>Process involved</i>	<i>Elastic scattering</i>	<i>Inelastic scattering</i>
1. Scattering by the undisturbed field of the atom in which the incident wave is only slightly disturbed.	Small intensity of scattering. Angular distribution monotonic, intensity decreasing with angle.	Angular distribution monotonic and decreasing more rapidly with angle than for elastic scattering.
2. Distortion of incident and scattered waves by atomic field.	Maxima and minima in cross - section - velocity curves (Ramsauer-Townsend effect). Maxima and minima in angular distributions, these being most marked for heavy atoms and disappearing at low velocities of impact.	No marked effect on cross-section - velocity curves. Maxima and minima in angular distributions at large angles, closely resembling the corresponding elastic angular distributions except for very low velocities of impact.
3. Electron exchange.	Apparent for light atoms (H, He) at low velocities of impact in producing greater variability of form in the angular distributions (i.e. He below 20 volts).	Leads to possibility of excitation of certain optically disallowed transitions (i.e. excitation of He triplets). Effect on angular distributions not yet known.
4. Disturbance of atomic field (polarization) or, alternatively, effect of interaction of scattered waves on each other.	Greatly increased scattering at small angles. Increase of total probability of an elastic collision.	Decrease of probability of an inelastic collision. Effect on angular distribution not yet known.

making a second collision with the same atom is increased. The effect of a second collision is to give rise to deviations of the character observed. Thus an electron may lose energy in exciting the atom when still at a considerable distance from it. In doing so it will suffer little deviation and in its subsequent course may regain the energy in a second interchange with the same atom, again without much deviation. The electron will eventually appear to an observer as having been elastically scattered through a small angle only. As a result there will be a reduction in the inelastic cross-section and an increase in the elastic scattering at small angles.

Again, the electron, after first suffering an inelastic scattering, may subsequently be diffracted by the atomic field. Alternatively, an electron in a diffracted beam which has hitherto suffered no energy loss may undergo an inelastic collision without subsequent deviation to an appreciable extent. Provided the proportional energy lost in an inelastic collision is small, the effect of either of these processes will be

to superimpose a diffraction pattern similar to that of the elastic scattering on the monochromatic, inelastically scattered electrons.

It appears that, in electron collisions with atoms, the interaction is just strong enough for these double processes to become appreciable in the slower encounters. In impacts of particles, both of atomic mass, the processes may become adiabatic, as far as energy interchange with electrons is concerned, because of the high probability of multiple processes during the long time the atoms spend under their mutual influence (see Chap. XII, §§ 3.3, 3.4). The highly concentrated and very strong forces between nuclear particles also make the one-body approximation completely inadequate for describing nuclear collisions except those between the lightest nuclei (see Chap. XIII, § 2).

XII

THE COLLISIONS BETWEEN MASSIVE PARTICLES

1. Physical phenomena involved

By 'Massive Particles' we mean particles of mass large compared with that of an electron, such as atoms, α -particles, etc. We arbitrarily exclude from consideration in this chapter collisions in which nuclear forces are involved. These will be dealt with in Chapter XIII.

Although the discussion of the phenomena which depend on collisions between massive particles is beyond the scope of this book, we give now a brief summary of these phenomena. A detailed description of the experimental technique involved and of the data obtained will be found in *Electronic and Ionic Impact Phenomena* by Massey and Burhop, Chapters VII and VIII.

1.1. *Passage of fast massive particles through matter*

Under this heading are included investigations of the ranges of α -particles, fast protons (*H*-particles), neutrons, and heavy nuclei in various materials. The method of investigation is either by actual observation of single particle tracks in a Wilson Cloud Chamber or by direct counting of particles by use of scintillations, valve amplification, or other methods. The theoretical problem here is to calculate the energy loss per cm. path through a given material as a function of the mass, energy, and charge of the particles, and the properties of the material. The development of such a theory is important, for observations of energy losses per cm. are often the only means of determining the nature or velocity of the particle.

1.2. *Capture or loss of charge on impact*

These phenomena are observed both for slow and fast positive ions. The behaviour of α -particles in this respect is discussed in Rutherford, Chadwick, and Ellis's book *Radiations from Radioactive Substances*, 1930, p. 119. Extensive experiments have also been carried out for slower ions.

1.3. *Transfer of excitation*

This phenomenon is very similar to the transfer of charge mentioned above, consisting in a transfer of electronic or other excitation from one of the colliding systems to the other. It is of considerable

importance in experimental physics, particularly in the excitation of spectra. The presence of small quantities of foreign gases often has a very pronounced effect on the intensity, or type, of the spectra produced in a discharge tube. An example is the well-known phenomenon of the quenching of resonance radiation.

The problem here is to evaluate the transition probabilities, particularly as functions of the energy differences of the two excited states.

1.4. *Elastic collisions of gas atoms*

The development of molecular ray technique has provided a powerful weapon for the investigation of the interaction of gas atoms. It has proved possible to demonstrate the wave nature of gas atoms by diffraction of beams of helium and hydrogen from crystal surfaces,† and the time is not far distant when investigations of the scattering of atoms by atoms under definite conditions of relative velocity will be a practical possibility. It is therefore of interest to calculate the effects to be expected in the elastic collisions of gas atoms.

The calculation of the collision cross-sections for gas atoms is also of interest in connexion with the theory of viscosity and of other transport phenomena in gases. Thus the variation of viscosity of a gas with temperature depends on the variation of a collision cross-section with relative velocity.‡

1.5. *Mobilities of positive ions in gases*

A very large number of determinations of the mobilities of ions in gases have been made,§ but it is only in recent years that the experimental conditions have been such as to render possible a clear understanding of the phenomena occurring. However, the recent experiments of Tyndall and others|| have shown that the purity of the gas under investigation is of vital importance. With gases containing even as little as 1 part in 10^6 of impurity, ion clusters are formed, with consequent slowing down of the ion. By high purification of the gases used (argon, helium, and neon) it has been possible to measure the mobilities of cluster-free ions in these gases. As the mobility is determined by the probabilities of collision between the gas atoms and the ions, it is possible to obtain valuable information regarding such collisions from these experiments.

† Cf. Fraser, *Molecular Rays*, 1931, Chap. 4.

‡ See § 3 of this chapter.

§ Thomson, *Conduction of Electricity through Gases*, 3rd ed., Cambridge (1928).

|| Tyndall, *Mobility of Positive Ions in Gases*, Cambridge (1939).

1.6. *Excitation of inner molecular motions*

Inelastic collisions between molecules, resulting in the excitation of rotation and nuclear vibration, are considered under this heading. At gas-kinetic velocities this is the only possible type of excitation. Direct experimental investigation of these effects, by methods similar to those used for collisions with electrons, is not yet possible; but indirect evidence as to the probabilities concerned is available from the following sources.

(a) *Measurement of accommodation coefficients.* The thermal accommodation coefficient of gas atoms on a solid surface is determined by the probability of energy exchange between the atoms and the vibrating atoms of the solid. From measurements of accommodation coefficients information may be obtained as to the magnitude of this probability and its variation with temperature.

(b) *The dispersion and absorption of high frequency sound.* A dependence of the velocity of high frequency sound on frequency was first observed by Pierce† in carbon dioxide. The cause of the dispersion, suggested first by Herzfeld and Rice‡, is the failure of the vibrational degrees of freedom of the gas molecules to follow the rapid temperature changes which occur during the passage of the supersonic disturbance. This is because the rate at which energy transfer occurs between vibration and translation is very low. The same effect gives rise to absorption due to the introduction of a phase difference between pressure and density fluctuations. A great amount of observational data is now available§ on dispersion and absorption in carbon dioxide and a great number of other gases and gas mixtures. From these data the chance of vibrational deactivation on impact is known for many molecules.

(c) *Reaction rates of unimolecular chemical reactions.* It is an empirical fact that an 'activation' energy is required before a unimolecular reaction will take place. In many cases this consists in the excitation of vibration, and the variation of reaction rate with the pressure of the decomposing gas or of foreign gases yields information as to the probability of activation of vibration by collision. Conversely, a theory of this excitation is of great value in interpreting the observations.

1.7. *Chemical reactions in general*

Under this heading are included a vast number of phenomena. The simplest type are two-body collisions, in which a rearrangement of

† *Proc. Am. Acad.*, Boston, **60** (1925), 11.

‡ *Phys. Rev.* **31** (1928), 691.

§ See, for example, Richards, *Rev. Mod. Phys.* **11** (1939), 36.

particles takes place on collision; but the most important type are three-body collisions, where combination or dissociation of two molecules takes place under the interaction of a third. The chief problem here is the calculation of the relative probabilities of different types of reaction in terms of the properties of the reacting substances.

This classification of the various phenomena, which come under the general title of collisions of heavy particles, is by no means a sharp one. The last four processes are of a very similar nature, but as the methods of experimental investigation are very different it was thought best to separate them as above.

Unfortunately the theory of collisions of heavy particles is at present not nearly so well developed as the theory of electronic collisions. Quantitative results are, at present, only available for fast collisions for which Born's first approximation is valid, and for the elastic collisions between gas atoms. However, a number of general results have been obtained for other cases, and for certain problems, such as the excitation of vibration, the only remaining difficulty is the complicated nature of the algebra. Following the same general scheme as for electronic collisions, we consider first the behaviour of fast particles.

2. Fast collisions of massive particles

2.1. *The stopping-power of matter for fast positive ions*

The calculation of the loss of energy per cm. path of fast positive ions traversing matter is very similar to the corresponding calculation for fast electrons, carried out in Chapter XI. We adopt the following notation:

M_1 , M_2 are the masses of the colliding and struck systems respectively.

$M = M_1 M_2 / (M_1 + M_2)$ is the reduced mass of the combined system. $Z'\epsilon$ is the charge on the ion.

The symbols k , k_n , κ , \mathbf{n}_0 , \mathbf{n} have the same meaning as in Chapter XI. The formulae of Chapter XI may be used with the mass of the electron replaced by M , and ϵ^2 by $Z'\epsilon^2$. The differential cross-section in momentum variables is thus†

$$I_{0n}(K) dK = \frac{128\pi^5 M^2 Z'^2 \epsilon^4}{k^2 \hbar^4} \frac{dK}{K^3} |\epsilon_{0n}(K)|^2, \quad (1)$$

where

$$\epsilon_{0n}(K) = \sum_{\sigma=-1}^N \int e^{i\mathbf{K}x_1} \psi_0 \psi_n^* d\tau,$$

and $K\hbar/2\pi$, as before, is the change of momentum. As before, the

† Cf. Chap. XI, eq. (10).

effective cross-section corresponding to excitation of the state n will be obtained by integrating the differential cross-section between the limits of allowed momentum change. For the fast collisions under consideration these limits are fixed by the same considerations as for electrons, since the matrix elements $\epsilon_{0n}(K)$ are the same functions of the momentum change $K\hbar/2\pi$ for both cases.

The lower limit of K will then be†

$$K_{\min} = 4\pi^2 M(E_n - E_0)/\hbar^2;$$

the upper limit is fixed by the conservation of momentum, so that

$$K_{\max} = 2km/(M+m) \simeq 2km/M. \tag{2}$$

Apart from these modifications the treatment is exactly the same as for electrons. We obtain the following formulae:

Excitation of optical levels:‡

$$Q_{nl,nr} = (16\pi^4 Z'^2 \epsilon^4/mv^2) |x_{nl,nr}|^2 \log\{2mv^2/(E_{nr} - E_{nl})\}. \tag{3}$$

Excitation of X-rays:§

$$Q_{nl}^i = (2\pi Z'^2 \epsilon^4/mv^2 |E_{nl}|) Z_{nl} b_{nl} \log(2mv^2/B_{nl}). \tag{4}$$

Primary ionization:||

$$Q_{nl} = (2\pi Z'^2 \epsilon^4 c_{nl} Z_{nl}/mv^2 |E_{nl}|) \log(2mv^2/C_{nl}). \tag{5}$$

Energy loss per cm. path:††

$$-\frac{dT}{dx} = (4\pi \epsilon^4 Z'^2 N/mv^2) Z \log(2mv^2/E), \tag{6}$$

where $E = 1.105Rh$, for hydrogen.

By comparison with the corresponding formulae for electrons given in Chapter XI in the sections listed below, we see that for high-velocity encounters a positive ion of charge $+\epsilon$ behaves in the same way as an electron moving with the same *velocity*. In the case of the energy loss per cm. path, there is a slight difference in the logarithmic term, which is $\log(mv^2/E)$ for an electron, but $\log(2mv^2/E)$ for a massive particle.

Table I gives a comparison‡‡ of the observed ranges of α -particles in hydrogen and helium with those calculated according to the formula (6). Thus we find that a particle traversing a gas containing N atoms/c.c. will, in losing velocity from v_1 to v_2 , move a distance R given by

$$R = [ME^2/(32\pi\epsilon^2 Z'^2 ZmN)][Ei(y_2) - Ei(y_1)], \tag{7}$$

† Cf. Chap. XI, § 1.1.

‡ Cf. Chap. XI, § 3.1.

§ Cf. Chap. XI, § 3.2.

|| Cf. Chap. XI, § 3.3.

†† Cf. Chap. XI, § 4.2.

‡‡ Williams, *Rev. Mod. Phys.* **17** (1945), 217.

TABLE I
Range of α -particles in Hydrogen and Helium

Gas traversed	Initial and final velocity (in 10^9 cm./sec.)		$\frac{\epsilon^2}{\hbar v}$	Distance travelled (cm.)		
				Observed	Bethe (Quantal)	Bohr (Classical)
Hydrogen	2.054	1.709	0.23	19.0	18.9	16.3
Hydrogen	1.709	1.802	0.25	15.8	16.2	13.7
Helium	2.054	1.709	0.26	22.6	22.3	18.4

where Z is the nuclear charge of the atoms through which the particle is passing and

$$y_1 = 2 \log(2mv_1^2/E), \quad y_2 = 2 \log(2mv_2^2/E),$$

$$Ei(y) = \int_{\infty}^y e^{-x} x^{-1} dx.$$

The agreement between the theory and experiment is seen to be good. Values calculated by means of Bohr's classical formula are also included. It is clear that they are less satisfactory than those given from (7). This is to be expected from the value of $\epsilon^2/\hbar v$ for the cases given. Following the same analysis as that given in Chap. XI, § 4.4, it is clear that the classical formula would only be preferred if $\epsilon^2/\hbar v \gg 1$.

A second condition for the validity of Born's approximation, which yields (6), was stated in Chap. XI, § 4.4, in the form $u^2/v^2 \ll 1$, where u is the orbital velocity of the atomic electrons. In considering the stopping-power of matter containing complex atoms the question arises as to whether this is to be interpreted as requiring that the positive ions concerned should be moving faster than even the K electrons. This is an important matter in dealing with the passage of positive ions as distinct from electrons. Thus, in order that an α -particle should be moving faster than the K electrons of, say, oxygen, it would have to possess an energy in excess of 800,000 e.V.

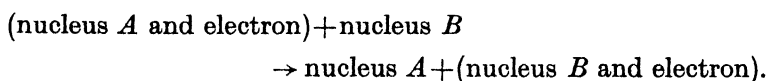
It was pointed out by Henneberg† that Born's approximation may be used for the calculation of energy loss even if the positive ion is moving slower than the K electrons, provided the nuclear charge $Z\epsilon$ of the atom is much greater than the charge $Z'\epsilon$ of the ion. This may be seen as follows. The appropriate method for dealing with collisions in which the relative motion of the colliding particles is slow compared with that of the internal motions is that of perturbed stationary states (P.S.S. method) (Chap. VIII, § 7). If the nuclear charge Z is $\gg Z'$, the

† *Zeits. f. Physik*, **86** (1933), 592.

perturbation of K electron wave functions by the ion will be small. It is shown in Chap. VIII, § 7, that, under these circumstances, the P.S.S. method gives the same result as Born's, apart from certain unimportant terms. Bethe† has made use of this extended range of validity of the formula (6) in deriving accurate semi-empirical data for the stopping-power of different materials towards protons, α -particles, etc. It must be remembered, however, that Born's approximation is not valid when $u^2/v^2 \gg 1$ if Z is not $\gg Z'$, i.e. for protons in hydrogen with energy $< 25,000$ e.V.

2.2. The capture of electrons by fast positive ions

The general theory necessary has been developed in Chapter VIII, this being a rearrangement collision in which the reaction is



Since we are dealing with fast collisions we may use Born's approximation and the formulae of Chap. VIII, § 4.2. The cross-sections for capture of an electron from state n around nucleus A to state q around nucleus B is given from Chap. VIII, eq. (45) by

$$Q_{nA \rightarrow qB} = \frac{v'}{v} \frac{8\pi^3 M^2}{h^4} \times \int_0^\pi \left| \iint V(\mathbf{r}_e, \boldsymbol{\rho}) \phi_q^*(\mathbf{r}_e) \psi_n(\mathbf{r}_e) \exp\{i(k\mathbf{n}_0 \cdot \mathbf{r} - k_q \mathbf{n} \cdot \boldsymbol{\rho})\} d\mathbf{r}_e d\boldsymbol{\rho} \right|^2 \sin\theta d\theta. \quad (8)$$

Here $V(\mathbf{r}_e, \boldsymbol{\rho})$ is the interaction energy between the nucleus A and the electron, $\psi_n(\mathbf{r}_e)$ is the wave function of the electron in the state n round nucleus A , $\phi_q(\mathbf{r}_e)$ is that of the same electron in the state q around nucleus B , $\boldsymbol{\rho}$ is the distance between the nucleus A and the centre of mass of the system (nucleus B +electron), and \mathbf{r}_e denotes the electronic coordinates. M is the reduced mass of the final system; if we denote the masses of the nuclei A and B by M_A , M_B respectively and the mass of the electron by m , then

$$M = M_A(M_B + m)/(M_A + M_B + m).$$

The wave numbers k , k_q are given by

$$k = \frac{2\pi v}{h} \frac{(M_A + m)M_B}{M_A + M_B + m}, \quad k_q = \frac{2\pi v'}{h} \frac{(M_B + m)M_A}{M_A + M_B + m}, \quad (9)$$

v , v' being the initial and final relative velocities. \mathbf{n}_0 , \mathbf{n} denote unit

† *Rev. Mod. Phys.* 9 (1937), 263.

vectors in the directions of initial and final relative motion, so that $\mathbf{n}_0 \cdot \mathbf{n} = \cos \theta$.

It is convenient to evaluate (8) by changing from the coordinates ρ, \mathbf{r}_e to the coordinates $\mathbf{r}_A, \mathbf{r}_B$ which denote the positions of the electron relative to the nuclei A, B respectively. We then obtain

$$Q_{n_A \rightarrow n_B} = \frac{v'}{v} \frac{8\pi^3 M^2}{h^4} \int_0^\pi \left| \int \int V(r_A) \phi_q^*(\mathbf{r}_B) \psi_n(\mathbf{r}_A) \times \right. \\ \left. \times \exp\left\{\frac{2\pi i}{h}(\mathbf{A} \cdot \mathbf{r}_A - \mathbf{B} \cdot \mathbf{r}_B)\right\} d\mathbf{r}_A d\mathbf{r}_B \right|^2 \sin \theta d\theta, \quad (10)$$

where $V(r_A)$ is written for $V(\mathbf{r}_e, \rho)$, and

$$(M_A + M_B + m)\mathbf{A} = M_A M_B v \mathbf{n}_0 - M_A (M_B + m) v' \mathbf{n}, \\ (M_A + M_B + m)\mathbf{B} = M_B (M_A + m) v \mathbf{n}_0 - M_A M_B v' \mathbf{n}. \quad (11)$$

Since the variables occurring in the double integrals are now separable, the calculation may be completed without difficulty if the atomic wave functions have a simple form.

The calculation of the cross-section $Q_{n_A \rightarrow n_B}$ for capture into a $1S$ state from a $1S$ state has been carried out by Brinkmann and Kramers using formula (10).† They find that if the velocity v is so high that the contribution to the cross-section comes only from small momentum changes,

$$Q = \frac{1}{2} 2^{18} \pi a_0^2 Z^5 Z'^5 s^8 [s^2 + (Z + Z')^2]^{-5} [s^2 + (Z - Z')^2]^{-5}, \quad (12)$$

where $s = hv/2\pi\epsilon^2$ and $Ze, Z'e$ are the nuclear charges. This expression shows that for high velocities the probability of capture falls off as v^{-12} , in sharp contrast to the excitation probability which, for optically allowed transitions, falls somewhat more slowly than v^{-2} (see formula (3) of this chapter). This is due to the presence in the capture problem of a term proportional to v in the minimum momentum change, due to the momentum involved in the electron transfer. No such term occurs in the case of direct excitation.

Since the experiments of Rutherford‡ and of Jacobsen§ refer to the capture of electrons by α -particles moving through air, Brinkmann and Kramers (loc. cit.) carried out the calculations approximately for capture from nitrogen atoms. They obtained reasonably good agreement with experiment, as is shown in Fig. 48. The empirical law found by Rutherford to represent the variation of the probability of capture with velocity, namely,

$$Q \propto v^{-5.6}, \quad (13)$$

† *K. Wet. Amst.* **33** (1930), 973.

‡ *Phil. Mag.* **47** (1924), 277.

§ *Ibid.* **10** (1930), 401.

is due to the fact that in the experimental range the probability of capture of a K electron increases with increasing velocity of the α -particle, whereas the cross-section for capture of an L electron decreases with nearly the 12th power of the velocity. The combination of the two effects leads to the law (13).

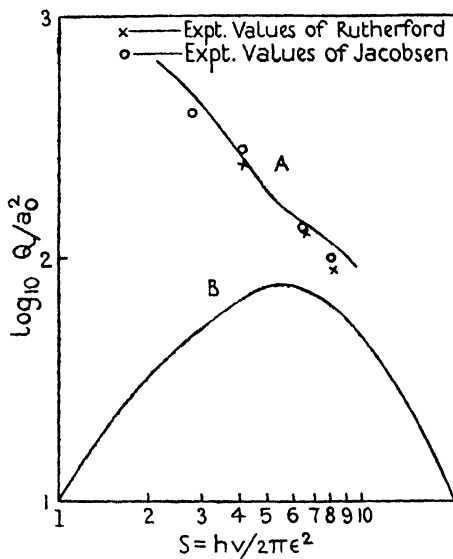


FIG. 48. Cross-sections for capture of electrons by α -particles.

A. Theoretical curve for nitrogen.

B. Theoretical curve for capture into a $1S$ state from a nucleus of charge 7.

2.3. The stopping-power of matter for fission fragments†

The nuclear fragments which result from fission of heavy nuclei (see Chap. XIII, § 6) possess an initial velocity of about 1.5×10^9 cm./sec. and an ionic charge of about 25ϵ . In order to obtain approximate expressions for the rate of energy loss by these fragments as they traverse different materials it is necessary to determine the effective ionic charge as a function of the velocity v of the ion.

At any particular velocity there will be a balance set up between the processes of capture and loss of electrons so that the mean charge on the ion will be $Z_{\text{eff}}(v)$. Provided the velocity of the fragment is large

† Bohr, *Phys. Rev.* **58** (1940), 654; *ibid.* **59** (1941), 270; *Kgl. Danske Vid. Selsk. Skr.* **18** (1940), 8; Lamb, *Phys. Rev.* **58** (1940), 696; Knipp and Teller, *ibid.* **59** (1941), 659.

compared with the orbital velocity u of the electrons in the atoms of the material through which the ions are passing, the rate of energy loss is then given by

$$\frac{dT}{dx} = -\frac{4\pi N Z_{\text{eff}}^2 \epsilon^4}{mv^2} \log \left(\frac{g_2 mv^3}{Z_{\text{eff}} E} \right). \quad (14)$$

Bohr's classical formula is used instead of Bethe's formula (6) because, over most of the range for which u^2/v^2 is small, $2\pi Z_{\text{eff}} \epsilon^2/hv$ is greater than unity (see Chap. XI, § 4.4).

The criterion adopted by Bohr for the determination of Z_{eff} depends

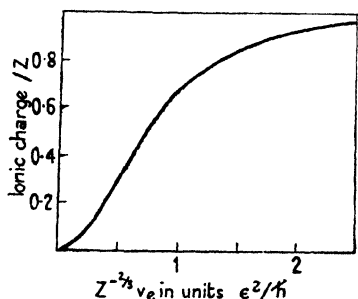


FIG. 49. Relation between degree of ionization and velocity of the most loosely bound electron, calculated by use of the Fermi-Thomas model.

on the result, illustrated clearly from the results of § 2.2, that capture of electrons into orbits in which the orbital velocity is less than the velocity of the ion is very improbable. On the other hand, the probability that an electron in an orbit with velocity greater than that of the ion will be lost by ionization will be small, the conditions being nearly adiabatic as far as the electron is concerned (see § 3.4).

It follows therefore that the most loosely bound electrons in the fragment will be those whose orbital velocity v_e is comparable with the ion velocity v , i.e. $v_e = \gamma v$, where γ is of order unity. If v_e is known, Z_{eff} may be determined.

The simplest way of relating Z_{eff} to v_e is to use the Fermi-Thomas field for an ion, as was done by Bohr† and by Knipp and Teller.‡ The latter authors obtained the relation illustrated in Fig. 49. As for the value of γ , Bohr† assumed that $\gamma = 1$, but Knipp and Teller‡ obtained a more accurate estimate empirically by analysing data available on the range in air of N^{14} , O^{16} , O^{17} , and F^{19} ions produced by nuclear disintegration. They found that γ should be taken between 1.5 and 1.9 for fission fragments in air.

As the velocity of the ion falls the effective nuclear charge decreases. The formula (14) becomes invalid when v falls below u , the velocity of the atomic electrons of the gas traversed, but, by then, the contribution to energy loss due to electron encounters has become so small that it is considerably exceeded by loss due to nuclear encounters. If M_1 is the mass of the fragment ion, M_2 of the gas atoms, Z_1 and Z_2 their respective

† Loc. cit.

‡ Loc. cit.

nuclear charges, then, due to nuclear encounters,

$$-\frac{dT}{dx} = \frac{4\pi M_1^2 v^2 M_2 N}{(M_1 + M_2)^2} \int_0^\pi \sin \frac{1}{2}\theta I(\theta) \sin \theta d\theta,$$

where $I(\theta)$ is the differential cross-section for a collision in which the angle of scattering in the centre of mass system is θ (see Chap. VIII, § 9).

Following the same procedure as in Chap. IX, § 6, we write, for $\theta > \theta_{\min}$, the Coulomb scattering formula

$$I(\theta) = \left\{ \frac{Z_1 Z_2 \epsilon^2 (M_1 + M_2)^2}{4 M_1 M_2 v^2} \right\}^2 \operatorname{cosec}^4 \frac{1}{2}\theta,$$

and ignore contributions from $\theta < \theta_{\min}$. θ_{\min} must be related to the effective screening distance a by the classical relation.

An estimate of a may also be made by means of the Fermi-Thomas model. In this way Bohr† found that

$$a \simeq a_0 (Z_1^{\frac{1}{2}} + Z_2^{\frac{1}{2}})^{-1}.$$

The relative importance of the contribution of electronic and nuclear collisions to the stopping in air of a fission fragment of mass number 94 and atomic number 37, with initial energy 100 M.e.V., is illustrated in Fig. 50. In this figure the 'stopping cross-sections' $N^{-1} dT/dx$ due to the two processes are shown as functions of the distance traversed, γ being taken as 1.5 throughout the range. It will be seen from the accompanying diagram, which gives the velocity of the fragment as a function of the distance traversed,

that the condition for validity of the expression (14), that v should be greater than the orbital velocity of the atomic electrons, is not satisfied towards the end of the range. However, as the nuclear effect begins to predominate here, it is probable that no important error is made.

2.4. Multiple scattering

The theory of multiple scattering of electrons has been discussed in Chap. IX, § 6. An exactly similar analysis may be applied to the

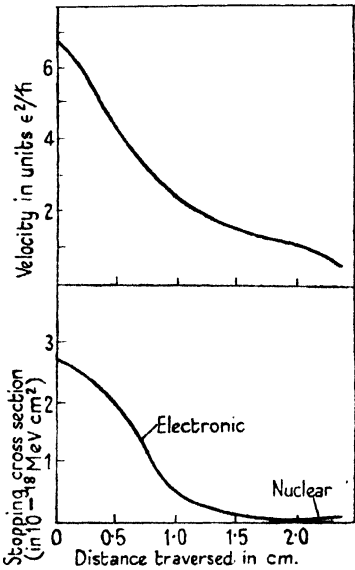


FIG. 50. Theoretical stopping cross-section for a typical fission fragment as a function of the distance traversed. Contributions from electronic and nuclear impacts are shown separately. The upper diagram gives the velocity of the fragment as a function of distance traversed.

† Loc. cit.

multiple scattering of charged massive particles. The mean square deflexion $\overline{\alpha^2}$ is given by $2\kappa \log(\frac{1}{2}\kappa/\theta_{\min})$,

where $\kappa = 4\pi N t Z_1^2 Z_2^2 \epsilon^4 (M_1 + M_2)^2 / \{M_1^2 M_2^2 v^4\}$.

N being the number of scattering nuclei/c.c., t the thickness of material $Z_2 \epsilon$, and M_2 the charge and mass of the scattering nuclei and $Z_1 \epsilon$ and M_1 the corresponding quantities for the incident particles, which possess a velocity v . For θ_{\min} we have

$$\theta_{\min} = 2 \cdot 10 Z_2^{\frac{1}{2}} \hbar (M_1 + M_2) / (M_1 M_2 v a_0) \quad (Z_1 Z_2 \epsilon^2 / \hbar v \ll 1), \quad (15)$$

$$= 3 \cdot 8 Z_2^{\frac{1}{2}} \epsilon^2 (M_1 + M_2) / (M_1 M_2 v^2 a_0) \quad (Z_1 Z_2 \epsilon^2 / \hbar v \gg 1). \quad (16)$$

Whereas for electrons wave conditions prevail corresponding to (15), for many cases in which massive particles are scattered the classical condition (16) is satisfied. Thus Table II, taken from a paper by E. J. Williams,† gives a comparison between observed and theoretical values of the most probable angle of scattering for α -particles scattered by foils of different materials. The classical formula (16) is seen to fit the observations better than the wave formula (15) as would be expected from the value of the discriminating parameter $Z_1 Z_2 \epsilon^2 / \hbar v$.

TABLE II
Multiple Scattering of α -particles

Scattering element	$\frac{Z_1 Z_2 \epsilon^2}{\hbar v}$	Most probable angle of scattering (degrees)		
		Observed	Classical theory	Born approximation
Gold	20	2.1	1.74	3.07
Tin	13	1.5	1.43	2.20
Silver	12	1.5	1.37	2.11
Copper	7	1.1	1.04	1.46
Aluminium	3	0.6	0.69	0.85

3. Slow collisions of heavy particles

3.1. *Elastic collisions of gas atoms*

As was pointed out in § 1.4 of this chapter, it is of considerable interest to calculate the collision cross-sections for gas atoms colliding with each other with gas-kinetic velocities. Besides the total elastic cross-section Q , which may now be measured directly by molecular ray methods,‡ we require also the cross-sections Q_η , Q_D which are effective

† *Rev. Mod. Phys.* 17 (1945), 217.

‡ Cf. Fraser, *Molecular Rays*, 1931, Chap. 4.

in viscosity and diffusion respectively. These are defined by†

$$Q_\eta = 2\pi \int_0^\pi I(\theta) \sin^3 \theta \, d\theta$$

$$Q_D = 2\pi \int_0^\pi I(\theta) \sin^2 \frac{1}{2} \theta \sin \theta \, d\theta,$$
(17)

where $I(\theta)$ is the scattered intensity in relative coordinates. These may be compared with

$$Q = 2\pi \int_0^\pi I(\theta) \sin \theta \, d\theta$$
(18)

[cf. Chap. II, eq. (18)].

The coefficient of viscosity η of a simple gas at absolute temperature T is then given by‡

$$\eta = \frac{5}{4j^3 M^2} \left(\frac{2\pi}{jM} \right)^{\frac{3}{2}} \frac{1+\epsilon}{\pi R_{11}},$$

where $j = 1/2\kappa T$, M is the mass of a gas atom, κ is Boltzmann's constant, and R_{11} is given by

$$R_{11} = \frac{1}{2} \int_{-\infty}^{\infty} v^7 Q_\eta e^{-\frac{1}{2} M v^2} \, dv;$$

v denotes the relative velocity of the gas atoms, of which Q_η as defined above is a function; ϵ is a small correcting term of order 10^{-2} .

Further, the coefficient of diffusion D between two gases (distinguished by suffixes 1 and 2) is given by

$$D = \frac{3}{16} \pi^{\frac{1}{2}} \left(\frac{M_1 + M_2}{j M_1 M_2} \right)^{\frac{7}{2}} \frac{1}{(\nu_1 + \nu_2) P_{12}} \frac{1}{1 - \epsilon_0},$$

where ν_1, ν_2 denote the numbers of each kind of atom per unit volume, M_1, M_2 are the masses of each kind of gas atom, ϵ_0 is a small correcting term§ depending on ν_1, ν_2 , and

$$P_{12} = 2 \int_{-\infty}^{\infty} v^5 Q_D \exp \left[-\frac{j M_1 M_2}{M_1 + M_2} v^2 \right] \, dv.$$

In order to investigate the modifications of the classical formulae which are introduced by the quantum theory it is simplest to start with the rigid sphere model for the gas atoms. We thus set for the

† *Vide* Massey and Mohr, *Proc. Roy. Soc. A*, **141** (1933), 434.

‡ Chapman, *Phil. Trans. A*, **216** (1916), 279; **217** (1917), 115. See also Massey and Mohr, *loc. cit.*

§ Chapman, *Phil. Trans. A*, **217** (1917), 115.

interaction energy between the spheres

$$V(r) = \infty \quad (r < r_0) \\ = 0 \quad (r > r_0).$$

On the classical theory this gives for Q the value πr_0^2 and for $I(\theta)$ the value $\frac{1}{4}r_0^2$. To calculate the scattering on the quantum theory the method of Chapter II may be applied (cf. Chap. II, § 5, where it is shown that in the low-velocity limit $Q \rightarrow 4\pi r_0^2$). If the colliding atoms are similar, account must also be taken of the symmetry relations

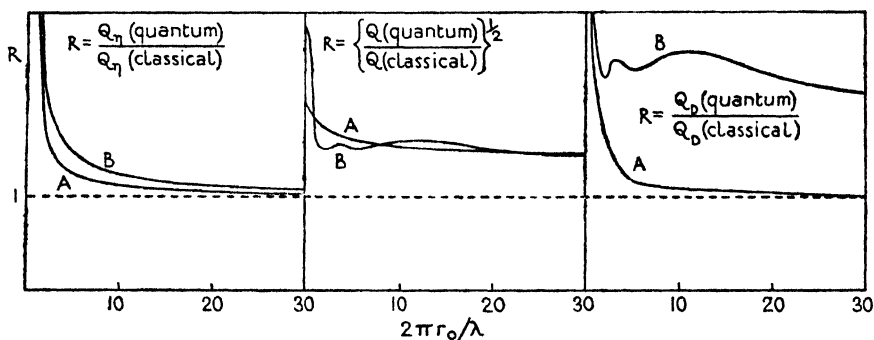


FIG. 51. Illustrating behaviour of quantum theoretical cross-sections effective in viscosity, scattering, and diffusion, on the hard sphere model.

Curves *A* refer to dissimilar atoms, *B* to identical atoms.

introduced by the Bose-Einstein statistics (cf. Chap. V). In this case $I(\theta)$ contains only even harmonics and so is symmetrical about $\theta = \frac{1}{2}\pi$. The exclusion of odd harmonics has the general effect of increasing the deviations from classical theory, as will be observed from Fig. 51, in which the quantum and classical values of Q , Q_η , and Q_D are compared.

It has already been pointed out (Chap. II, § 5) that, as the ratio of wave-length to atomic diameter tends to zero, the total cross-section Q tends, not to its classical value, but to twice that value. The additional scattering which gives rise to this doubling is confined to smaller and smaller angles θ as the wave-length decreases. The contribution of this scattering to the viscosity and diffusion cross-sections therefore becomes less and less important owing to the additional factors, proportional to θ^2 for small θ , with which the differential cross-section $I(\theta)$ has to be weighted. We therefore find that, unlike Q , both Q_η and Q_D tend to the classical limits as the wave-length decreases. At small values of $2\pi r_0/\lambda$ there is a considerable departure from classical behaviour apparent in all these cross-sections. This modifies the temperature dependence of the viscosity η at low temperatures. According to the

classical theory, with the rigid sphere model, $\eta \propto T^{-1}$ as $T \rightarrow 0$. With the quantum theory the variation is more rapid.†

Deviations from classical behaviour are to be expected at temperatures below 50° K in helium and 100° K in hydrogen. Quantal calculations of the viscosity to be expected for helium have been carried out by several authors‡ on the assumption of different interaction laws between helium atoms. The usefulness of this technique for determining the true interaction law may be supplemented by a similar discussion of the second virial coefficient, the quantum formula§ for which depends on the same phases η_n which determine the scattering cross-sections. More observed results are necessary before this programme can be completed.

The total cross-section Q can be measured in principle by molecular ray methods, but a very high angular resolving power is necessary to obtain a value independent of the smallest deviation recorded as a collision. For further details of this work see Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chapter VII.

3.2. *Transfer of excitation and of charge in slow collisions*

The importance of the transfer of excitation between atoms on collision has already been mentioned at the beginning of this chapter. The general feature which emerges from the experimental data is that the probability of this transfer is a maximum when the energy difference between the two states is zero. The energy difference appears to be usually more important in determining the probability of the transfer than the relative velocities or nature of the systems concerned. As an illustration of this we shall consider the results of a few selected experiments.

3.21. *Quenching of mercury resonance radiation.* It is well known that the presence of a foreign gas in a mercury resonance lamp has the effect of diminishing the intensity of resonance radiation. This is due to the deactivation of the excited mercury atoms by collision with molecules of the foreign gas. From observations of the variation in intensity of the resonance radiation with different foreign gases present it is possible to determine the effective cross-sections corresponding to deactivation of the mercury atoms by the gas molecules. Such a series of observations was carried out by Zemansky;|| in Fig. 52(a) the relative

† Massey and Mohr, loc. cit.

‡ Massey and Mohr, *Proc. Roy. Soc. A*, **144** (1934), 188; Massey and Buckingham, *ibid. A*, **168** (1938), 378; **169** (1938), 205; Buckingham, Hamilton, and Massey, *ibid. A*, **179** (1941), 103; de Boer and Michels, *Physica*, **6** (1939), 409.

§ Uhlenbeck and Beth, *ibid.* **3** (1936), 729; Gropper, *Phys. Rev.* **51** (1937), 1108.

|| *Ibid.* **36** (1930), 919.

efficiencies of different gases in producing the transition $2^3P_1 \rightarrow 2^3P_0$ of the mercury atom, which requires 0.218 volts, are illustrated. The efficiency is given in terms of the effective cross-section, and is plotted against the energy of the vibrational level of each gas with energy nearest to the resonance value 0.218 volts. It is clear that the points obtained determine a resonance curve of the usual type. Carbon monoxide alone behaves anomalously, showing that the energy difference is not the only factor concerned.†

3.22. *Excitation of sodium by excited mercury atoms.* Experiments of a somewhat similar nature were carried out by Beutler and Josephy,‡ who irradiated a mixture of sodium and mercury vapours with a mercury lamp and measured the intensity of the sodium lines with excitation energies in the neighbourhood of that of the exciting line (wave-number 2537). Allowing for the statistical weight of the terms involved in the sodium lines, they obtained the curve illustrated in Fig. 52(b) for the excitation probability of the different sodium levels represented as a function of the energy of the level. A strong maximum is observed at the resonance point with a subsidiary maximum corresponding to resonance with the metastable 2^3P_0 state of mercury.

3.23. *The absorption of positive ions.* 'Umladung.' The observed absorption of slow positive ion beams in gases is due almost entirely to neutralization by capture of electrons from the gas molecules. A large number of measurements of the absorption coefficients of ions in gases have been carried out by various investigators and in all cases the absorption coefficient is found to be greatest for ions of the same gas; that is to say, positive ions are absorbed most strongly by gases which form the same ions by loss of an electron.

The most extensive measurements are due to Wolf,§ and Fig. 52(c) illustrates clearly, from his results, the resonance character of the phenomena.

A great number of other examples of this phenomenon are known,|| and it is clearly of great importance in chemical kinetics and in spectroscopy.

We now consider these phenomena from a theoretical point of view.

† Doubt has recently been thrown on the resonance character of the quenching process (Laidler, *J. Chem. Phys.* **10** (1943), 43), as the hydrocarbons quench by chemical action.

‡ *Zeits. f. Physik*, **53** (1929), 755.

§ *Ann. der Physik*, **23** (1935), 285 and 627; **25** (1936), 737; **27** (1936), 543; **29** (1937), 33; **30** (1937), 313.

|| Cf. Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chapters VII and VIII.

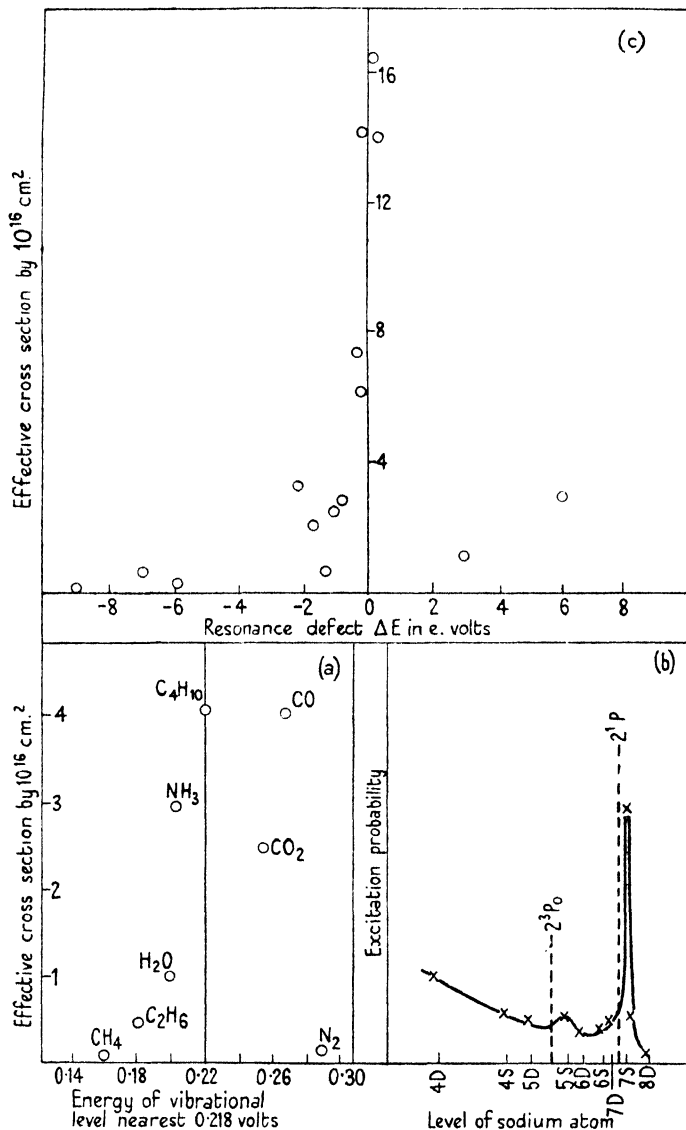


FIG. 52. Illustrating resonance phenomena in collisions between atoms or ions in which transfer of excitation or of charge is involved.

- (a) Relative efficiencies of various gases in quenching mercury resonance radiation.
- (b) Excitation probabilities of various sodium lines by collisions of the second kind with mercury atoms excited to the 2^1P state. Dotted lines indicate energies of the 2^1P and 2^3P_0 states of mercury.
- (c) Cross-sections for transfer of charge between various ions (of 400 e.V. kinetic energy) and neutral molecules as a function of the resonance defect ΔE (ΔE is taken positive when the relative kinetic energy is increased by the charge transfer).

3.3. Theory of resonance effects

In Chap. VIII, § 6, a method of calculation of cross-sections for transitions between two states in approximate resonance was discussed. We use the same notation in this section, and denote the initial state by the suffix 0 and the final state by the suffix n . In the two following cases it was shown that the problem consists in the solution of two simultaneous differential equations only. If the states 0 and n are in approximate resonance, or if the interaction energy terms V_{st} are small for all states s and t , the probability of the transition is determined by the functions F_n^l which are proper solutions of the simultaneous equations

$$\left[\frac{d^2}{dr^2} + k^2 - U_{00} - \frac{l(l+1)}{r^2} \right] F_0^l = U_{0n} F_n^l,$$

$$\left[\frac{d^2}{dr^2} + k_n^2 - U_{nn} - \frac{l(l+1)}{r^2} \right] F_n^l = U_{0n} F_0^l.$$

F_0^l , the component of the incident and elastically scattered wave, has the asymptotic form

$$F_0^l \sim k^{-1}(2l+1)\exp(i\eta_0^l) i^l [\sin(kr - \frac{1}{2}l\pi + \eta_0^l) + g_0^l \exp\{i(kr - \frac{1}{2}l\pi + \eta_0^l)\}].$$

F_n^l corresponds to an outgoing wave only, having the asymptotic form

$$F_n^l \sim k_n^{-1}(2l+1)q_n^l \exp(ik_n r).$$

The cross-section for the inelastic collision is then given by

$$Q_n = \frac{4\pi}{kk_n} \sum (2l+1) |q_n^l|^2.$$

For collisions involving transfer of excitation the form of U_{0n} depends on whether the transitions in the two systems A and B are optically allowed or not. If they are associated with multipole moments of order p and q respectively, then, ignoring angular variations,

$$U_{0n}(r) \sim a/r^{p+q+1}. \quad (19)$$

Thus, if both transitions are optically allowed,

$$U_{0n}(r) \sim a_3/r^3, \quad (20)$$

while, if the transitions are of $S \rightarrow S$ type or involve electron exchange, the moment vanishes to any order and

$$U_{0n}(r) \sim a_0 e^{-\lambda r}. \quad (21)$$

It follows that, in many cases, the coupling potential U_{0n} falls off quite slowly with distance at large distances and will be much larger than U_{00} or U_{nn} there. Exceptions will be cases such as (21) and also collisions between ions and atoms, or between two ions, for which U_{00} or U_{nn} may

fall off quite slowly with distance. Stueckelberg† has shown that, if a real crossing-point R exists at which

$$k^2 - k_n^2 - U_{00} + U_{nn} = 0,$$

then the maximum cross-section is of order πR^2 . On the other hand, if no such point exists, the critical distance R_1 is that for which

$$|U_{0n}(R_1)| \simeq |k^2 - k_n^2 - U_{00} + U_{nn}|,$$

and cross-sections of order πR_1^2 may arise. In view of the long range of U_{0n} for such cases as (20), it is clear that R_1 may often be considerably greater than R . Stueckelberg† has therefore considered in detail the cross-section to be expected when U_{0n} has the form α/r^s for large r .

In these cases the critical distance R_1 will be so large if the resonance defect ΔE is small, that U_{00} and U_{nn} may be ignored there, giving

$$R_1 = \left(\frac{\beta}{\Delta E} \right)^{1/s},$$

where $\beta = \alpha \hbar^2 / 2m$. The formula obtained for $|q_n^l|^2$ depends on whether l is $>$ or $<$ l_0 , where

$$k^2 - U_{00}(R_1) - \frac{l_0(l_0 + 1)}{R_1^2} = 0.$$

When l is $<$ l_0 , (22)

$$|q_n^l|^2 = \frac{k_n}{k} e^{-2\delta} (1 - e^{-2\delta}) \sin^2 \tau,$$

a formula of the same form as for the crossing-point case (Chap. VIII, eq. (77)), but now

$$\delta = M_s \left(\frac{U_{0n}^2}{f_{\dagger} U'_{0n}} \right)_{r=R_1}, \tag{23}$$

where

$$2f = f_0 + f_n + 2(f_0 f_n - U_{0n}^2)^{\dagger},$$

$$f_{0,n} = k_{0,n}^2 - l(l+1)/r^2,$$

and M_s is a quantity of order unity which depends only on s . Except for $l \simeq l_0$, U_{0n} will be negligible compared with f_0 or f_1 and we have

$$\delta \simeq \frac{4\pi}{\hbar v_l} \frac{M_s}{s} (\Delta E)^{(s-1)/s} \beta^{1/s}, \tag{24}$$

where v_l is the relative velocity of the colliding systems at the critical point. Just as for the crossing-points case discussed in Chapter VIII, adiabatic conditions, corresponding to large δ , prevail when the interaction U_{0n} is large and the relative velocity small at the critical distance.

For $l > l_0$ Born's approximation may be used to calculate $|q_n^l|^2$, the interaction U_{0n} being small over the effective range $R_1 < R < \infty$ within which the systems, with the particular relative angular momentum,

† *Helv. Phys. Acta*, 5 (1932), 370.

approach. In collisions between atoms both l and kR_1 will be very large and it is then found that

$$|q_n^l|^2 = \frac{k_n}{k} \frac{\pi^2 \alpha^2 l^2 c_1}{16} \left(\frac{k}{2l}\right)^{2s-4} \left\{1 + c_2 l \frac{\Delta E}{E_0}\right\}^{s-2} \exp\left\{-l \frac{\Delta E}{E_0}\right\}, \quad (25)$$

where

$$c_1 = \{\Gamma(s-1)\}^2 / \{\Gamma(\frac{1}{2}s)\}^4, \quad c_2 = [\Gamma(\frac{1}{2}s) / \Gamma(s-1)]^{2(s-2)}.$$

The total cross-section Q_n may now be calculated approximately, as

$$Q_n = \frac{8\pi}{kk_n} \int_0^\infty l |q_n^l|^2 dl,$$

where, for $l < l_0$ formula (22) is used and for $l > l_0$ formula (25).

In this way Stueckelberg finds that

$$Q_n = \pi \left(\frac{\beta}{\Delta E}\right)^{2/s} f(\Delta E^{(s-1)/s} \beta^{1/s} v^{-1} \hbar^{-1}), \quad (26)$$

where

$$\begin{aligned} f(x) &= 8M_s x/s && (x \ll 1), \\ &= 32c_1 c_2^{s-2} x^{s-1} e^{-2x} && (x \gg 1), \end{aligned}$$

and is illustrated for the case $s = 3$ in Fig. 53.

Close to resonance we see that

$$Q_n \rightarrow \frac{8\pi}{s} M_s \Delta E^{(s-3)/s} \beta^{3/s} / (\hbar v).$$

In the important case, $s = 3$, the cross-section tends to a constant value as resonance is approached, and the variation with ΔE is of true resonance type. Fig. 54 illustrates the variation of Q_n with ΔE for $s = 3$, taking $\beta = e^2 a_0^2$, $m = 10$ atomic units, and a velocity corresponding to an energy of 1 e.V. The sharp resonance is obvious, as well as the large magnitude of the cross-section near resonance.

The variation of Q_n with relative velocity for different values of ΔE is also of interest. Referring to (26) and Fig. 55 it will be seen that, for small velocities, the variation will be like $v^2 \exp(-a/v)$, where $a = 2\Delta E^{2/3} \beta^{1/3} / \hbar$, reaching a maximum of order $\pi(\beta/\Delta E)^{2/3}$ for a velocity of order $(\beta\Delta E^2)^{1/3} / \hbar$, and then falling off as v^{-1} at higher velocities. Typical examples are illustrated in Fig. 55.

For higher values of s the general behaviour is similar except that the cross-section vanishes in the limit of exact resonance. However, it reaches a maximum very close to resonance if the relative velocity is small and falls off rapidly thereafter as the energy defect ΔE increases.

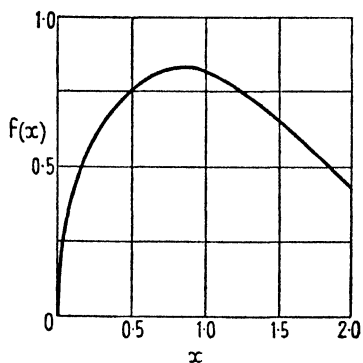


FIG. 53.

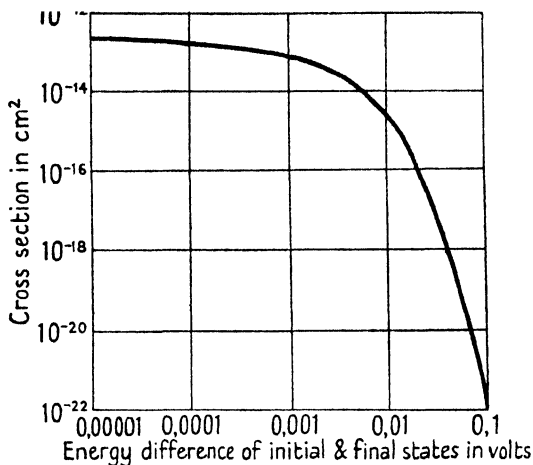


FIG. 54. Calculated cross-section for transfer of charge between two atoms as a function of the resonance defect ΔE .

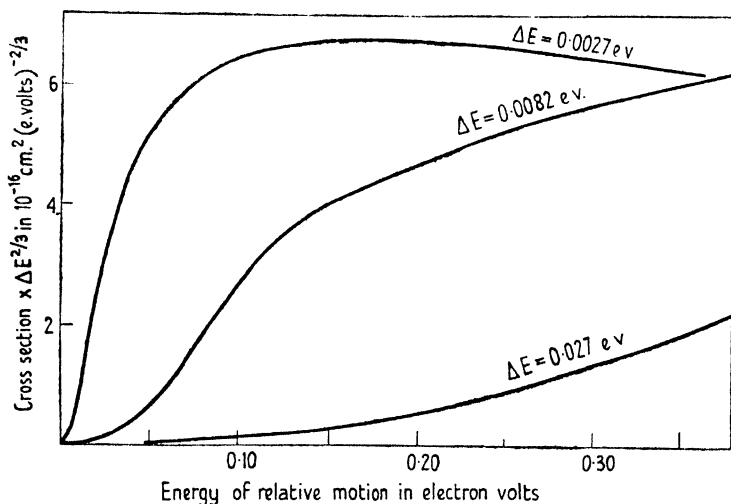


FIG. 55. Variation of cross-section for transfer of excitation with energy of relative motion for different resonance defects ΔE . β is taken as $e^2 a_0^2$ and m as $10m_H$, as in Fig. 54.

The maximum cross-section will fall off as s increases owing to the reduced range of the coupling energy V_{0n} .

Electron exchange will normally involve collision between an ion and an atom or between two ions. In these cases V_{0n} falls off much more rapidly with distance than V_{00} or V_{nn} and the crossing-point formulae are applicable. If the collision is between an ion and an atom, V_{00} will behave

asymptotically as $\alpha\epsilon^2/r^4$, where α is the polarizability of the atom. The crossing point will be given approximately by

$$R = \left(\frac{\alpha\epsilon^2}{\Delta E} \right)^{\frac{1}{4}}.$$

Although R may be made as large as one pleases by taking ΔE small enough, the rapid fall of V_{0n} with r makes the probability of transfer at the crossing point very low, as will be seen from (79) Chap. VIII, § 6.2. The resulting cross-section will not then be of order πR^2 but much smaller.† It will nevertheless exhibit resonance characteristics similar to those for the cases discussed above in which $s > 3$, i.e. a maximum not at exact resonance but close to it.

For collisions between a positive and negative ion, in which mutual neutralization occurs by electron transfer, the crossing point may occur at very large $R (= \epsilon^2/\Delta E)$, when ΔE is small, but the cross-section will normally be very much less than πR^2 owing to the small value of V_{0n} at the crossing point. In this case also the maximum cross-section does not occur at exact resonance, but may be replaced quite considerably from it.‡

Summarizing we may say that the largest maximum cross-section (much greater than gas kinetic) and the sharpest resonance should be expected for transfer of excitation involving optically allowed transitions in both systems. Resonance, with the maximum slightly displaced from the position $\Delta E = 0$, would be expected in most other cases, but the maximum cross-section is not likely to be nearly as large.

3.4. *Passage of positive ions through gases*

In this section we consider the collisions of positive ions of energy greater than, say, 50 volts with gas atoms. The types of collision which occur may be classified as follows:

1. Elastic collisions.
2. Collisions resulting in the neutralization of the ion by electron capture from the gas atoms.
3. Inelastic collisions resulting in excitation or ionization either of the gas atoms or the incident ions.

The cross-section for elastic collisions must be calculated by the Method of Partial Cross-sections (Chap. II, § 1) and is given in terms

† It may indeed be so small that the major contribution comes from a second crossing point at a much smaller value of R (of order 10^{-8} cm.) where V_{0n} is appreciable.

‡ Bates and Massey, *Phil. Trans. Roy. Soc.* **239** (1943), 269.

of the phase constants by the series

$$Q = \frac{4\pi}{k^2} \sum_n (2n+1) \sin^2 \eta_n. \quad (27)$$

k is, as usual, equal to $2\pi/\text{wave-length}$. A large number of terms of this series are required (at least 400 for 100 volt protons in helium); but the summation over a certain range of n may be replaced by an integral. Use may also be made of the oscillatory nature of $\sin \eta_n$ when n is small (less than 200 for 100 volt protons in helium). Some calculated values of Q for the collisions of protons with helium and argon are given in Table III.

TABLE III

Gas	Proton energy in e.V.	Cross-section in units of πa_0^2	Gas kinetic cross-section in units of πa_0^2 (exptl.)
He	90	3.7	2.6
	800	2.0	
A	73	16.4	7.3
	650	10.7	

It will be seen that these calculated cross-sections do not differ greatly from the gas-kinetic values; yet experimental determinations† of the free paths of protons in both helium and argon have indicated much smaller total cross-sections than the gas-kinetic. However, the reason for this is clear when the angular distribution of the scattered protons is considered. This may be calculated by classical methods‡ except at very small angles of scattering, and it may be shown that the limiting value of the angular distribution function $I(\theta)$ for zero angle of scattering is approximately $\frac{1}{4}k^2Q^2$ which is $\gg Q$ except for very slow ions ($< \frac{1}{10}$ volt). Combining these results it is found that the scattered intensity falls off so rapidly with increasing angle of scattering that only a small fraction of the elastic collisions occurring could be observed in the experiments cited.

Collisions in which an electron is captured by the ion are usually inelastic, as the mutual kinetic energy is altered by the collision. In the special case of exact resonance which occurs, for example, when a helium positive ion captures an electron from a helium atom, the collisions are elastic in the sense that the mutual kinetic energy remains unaltered. It is not strictly correct to assign a cross-section for charge

† Dempster, *Phil. Mag.* 3 (1927), 115; Ramsauer, Kollath, and Lilienthal, *Ann. der Phys.* 8 (1931), 709.

‡ Cf. Chap. VII, §§ 4, 5 for the proof of this statement.

transfer in the case of exact resonance, as it is impossible to determine experimentally whether an ion observed in any given direction is the incident ion which has been scattered or a struck atom which has lost an electron. Actually the observations show that large numbers of positive ions are produced moving in directions nearly perpendicular to the incident beam. As we know from experiments in which the incident ions are distinguishable from atoms which have lost an electron, that very few ions are directly scattered in such directions, we may arbitrarily consider that all ions which move in directions making angles greater than, say, 45° with the direction of incidence, are struck atoms which have lost one electron, all the remaining ions arising by direct scattering from the incident beam. Since the observed absorption of, say, He^+ ions in He is mainly due to large angle deviations, we may say, on the basis of our assumption, that the absorption is mainly due to charge transfer. To calculate the absorption cross-section we may then use the formula given in Chap. VIII, § 6.1, for the limiting value of the probability of an inelastic collision in the case of exact resonance. This calculation follows on the same lines as that of the elastic cross-section given earlier in this section, and it is found that the absorbing cross-section due to transfer of charge is comparable with the gas-kinetic cross-section, in agreement with the experiments of Kallmann and B. Rosen.† A more exact theory, which takes account of the identity of the nuclei (cf. Chap. V) will only modify the form of the angular distribution of the scattered ions at intermediate angles of scattering, where maxima and minima will occur due to the interference of the two types of scattered waves. Since the contribution to the cross-section arising from these angles is very small, this effect is unimportant, except for precise measurements of angular distributions.

When electron capture requires change of kinetic energy, the theory of the process must follow on exactly similar lines to that of excitation and ionization by the ions. Since the velocity of the ions is small compared with the orbital velocities of the atomic electrons, and since there are few cases where the resonance between initial and final states is so close as to permit of the consideration of the interaction of these two states alone, the only method which is satisfactory for the discussion of these processes is the Method of Perturbed Stationary State Wave Functions discussed in Chap. VIII, § 7.

This method has been applied to the calculation of the cross-sections for excitation of the 2^1P state of helium by protons and for electron

† *Zeits. f. Physik*, **64** (1930), 808.

capture from helium by protons.† The impact parameter formulation of the method has also been applied by Frame‡ to calculate the cross-section for the excitation of the $(1s)^23p^2P$ state of lithium by slow α -particles. Fig. 56 illustrates his results. For purposes of contrast the corresponding curve for electron is also included in the figure. The obvious difference in the calculated behaviour of the two particles is shown also by the experimental results, both for excitation and ionization.

Comparison of the theoretical cross-section-velocity curve with the

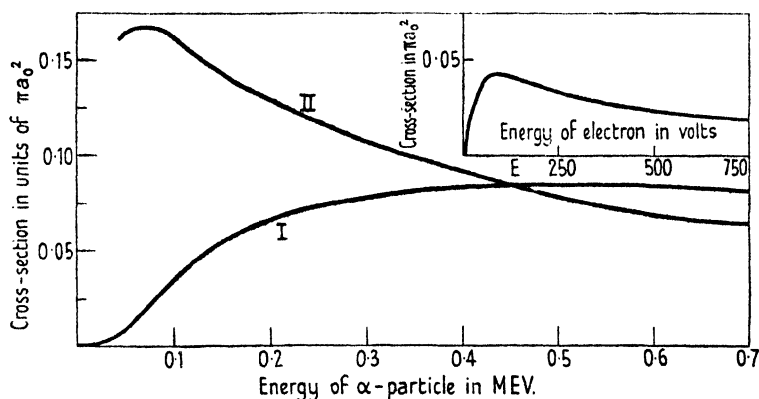


Fig. 56. Calculated cross-section for excitation of the $(1s)^23p$ level of lithium by α -particles.

I. Using perturbed stationary state method in the impact parameter form.

II. Using Born's approximation.

Inset figure gives the corresponding cross-section for excitation by electrons, calculated by Born's approximation.

corresponding curves for transfer of excitation (Fig. 55) reveals a close similarity. In both cases the cross-section decreases rapidly from the maximum as the velocity falls, owing to the approach to adiabatic conditions. The maximum occurs when the relative velocity is comparable with the orbital velocity of the atomic electrons concerned. The steepness of the fall from the maximum as the velocity decreases is greater the greater the resonance defect ΔE . As a rough approximation the velocity variation of the cross-section in the near adiabatic region may be written

$$C \exp(-a/v),$$

where a increases with ΔE . Qualitative evidence in favour of this dependence on ΔE is provided by numerous experiments on excitation

† Massey and Smith, *Proc. Roy. Soc. A*, **142** (1933), 142.

‡ *Proc. Camb. Phil. Soc.* **33** (1937), 115.

by slow ions. Thus Appleyard† showed that sodium ions with energy between 300 and 3,000 e.V. can excite mercury atoms ($\Delta E = 5$ e.V.), but are not appreciably excited themselves (requiring $\Delta E = 32$ e.V.). Again Döpel‡ has found that hydrogen atoms with less than 1,000 e.V. energy can excite potassium and sodium atoms ($\Delta E = 2$ e.V.) quite strongly, although even when their energy is increased to 20,000 e.V. there is no indication that they are ever excited themselves by the collision (requiring $\Delta E = 10$ e.V.).

The strong reduction of the cross-section by the approach to adiabatic conditions is not given adequately by Born's approximation except in certain very special circumstances. This is revealed by comparing curve II of Fig. 56 given by Born's approximation with that, I, given by the perturbed stationary state method. Cases where the two methods agree have been mentioned in § 2.1.

Although there is qualitative agreement between theory and experiment as far as these phenomena are concerned, much remains to be done yet before even semi-quantitative prediction of cross-sections for ionization and excitation by slow positive ions can be made. For further details of existing experimental data and their interpretation the reader is referred to Massey and Burhop, *Electronic and Ionic Impact Phenomena*, Chapters VII and VIII.

3.5. *Exchange of energy between translational motion and molecular vibration and rotation*

In this section we shall discuss methods by which one may calculate the probability that a molecule will change its vibrational or rotational state under impact from another atom. For this purpose we require to know the interaction energy between the molecule and atom.

The theoretical treatments given at present have been confined to impacts in which the striking atom moves along the line joining the nuclei of a diatomic molecule; the vibrational transition probabilities will probably be greatest for such impacts. We need, then, only consider the interaction of the striking atom with one of the atoms of the molecule (of mass M_B , say). A form of the interaction energy which probably gives a very good approximation near the distance of closest approach is

$$Ce^{-ar}, \quad (28)$$

where r is distance between the atom M_B and the striking atom. The constant a may be determined by comparing (28) with the potentials

† *Proc. Roy. Soc. A*, **128** (1930), 330.

‡ *Ann. der Phys.* **16** (1933), 1.

deduced by Lennard-Jones† from experimental measurements of the viscosity and thermal conductivity of gases.

If we denote by R the distance between the nuclei of the striking atom and the centre of gravity of the molecule, and by ρ the distance between the vibrating nuclei of the molecule, then (28) may be written

$$V(R, \rho) = e^{-\alpha(R+\lambda\rho)}, \quad (29)$$

where

$$\lambda = M_C/(M_B + M_C),$$

and M_C is the mass of the other nucleus in the molecule. If we assume that the vibration is simple harmonic, the vibrational wave functions are Hermite polynomials. Owing to the fact that the amplitude of the nuclear vibration is small compared with the length $1/a$, the non-diagonal matrix elements of V with respect to the vibrational wave functions are small. The method of Chap. VIII, § 5 (perturbation method with distorted waves), may thus be used to calculate the transition probabilities with considerable accuracy.

Such calculations have been carried out by Zener‡ using a simplified field, and by Jackson and Mott§ using the field (29). With the latter field the following results are obtained for a head-on collision such as that described. We denote by $p_{n,m}$ the probability per collision that the vibrational quantum number changes from n to m ; M_A is the mass of the striking atom, v_n the relative velocity before the collision, v_m afterwards. Then

$$p_{n,m} = \frac{32\pi^4}{\hbar} \frac{M_C(M_B + M_C)M_A^2}{a^2 M_B(M_A + M_B + M_C)^2} (n + \frac{1}{2} \pm \frac{1}{2}) \nu \times \\ \times \frac{\sinh \pi q_n \sinh \pi q_m}{(\cosh \pi q_n - \cosh \pi q_m)^2} \quad (m = n \pm 1),$$

where

$$q_n = 4\pi M^* v_n / \hbar a, \\ q_m = 4\pi M^* v_m / \hbar a, \\ M^* = M_A(M_B + M_C) / (M_A + M_B + M_C),$$

and ν is the natural frequency of the vibrator. The probability of an energy change in which n changes by more than 1 is very small, except for high energies of impact.

The chief interest of this formula is that it shows that exchange of energy between translation and vibration takes place only with difficulty. Thus in the one-dimensional collisions of helium with nitrogen

† R. H. Fowler, *Statistical Mechanics*, Ch. X, 1929. ‡ *Phys. Rev.* 37 (1931), 556.

§ Jackson and Mott, *Proc. Roy. Soc. A*, 137 (1932), 703.

at room temperature, the probability of deactivation of the molecule from the first vibrational state is of the order 6×10^{-7} . It is the very low probability of exchange of vibrational and translational energy which accounts for the dispersion and absorption of high frequency sound in various gases.†

Similar methods may be applied to the consideration of the transfer of excitation of vibration between two molecules on impact. It is found then that, even in the case of exact resonance, the probability of transfer of vibrational energy may be very small. The resonance cross-section increases with the reduced mass of the two molecules and the kinetic energy of relative motion, while the resonance effect is sharpest for heavy molecules.

Rice‡ has applied the theory to the consideration of the activation of various complex molecules by impact with similar molecules, with inert gas atoms, and with hydrogen. He finds that hydrogen is as efficient in activation as these molecules, and is much more so than the inert gases. This is in general agreement with the chemical evidence.

The method has also been applied successfully to the theory of the accommodation coefficient of a solid surface for gas atoms.§ This coefficient is determined by the rate of interchange of translational energy of the incident atoms with energy of vibration of the solid lattice.

The theory of the excitation of rotational motion is less well developed, but it appears that transfer of energy between translation and rotation can take place relatively easily.|| For a detailed account of the various aspects of vibrational and rotational energy exchange between molecules reference should be made to the review articles by Hiedemann††, Richards‡‡ Oldenburg and Frost§§, and to Chapter VII of *Electronic and Ionic Impact Phenomena* by Massey and Burhop.

3.6. Chemical reaction rates

Although the combination of two atoms A , B to form a molecule AB , giving up their surplus energy to a third atom C , can be regarded as the inverse of a process of excitation of a continuous vibrational state of the molecule AB by the atom C , no attempt has yet been made to

† Cf. § 1.5 of this chapter.

‡ *Chemical Reviews*, **10** (1932), 125.

§ Jackson and Mott, *Proc. Roy. Soc. A*, **137** (1932), 703; Jackson and Howarth, *ibid.* **142** (1933), 447; **152** (1934), 515.

|| Zener, *Phys. Rev.* **37** (1931), 556; Roy and Rose, *Proc. Roy. Soc. A*, **149** (1935), 511.

†† *Ergebnisse d. Exakt. Naturwiss.* **14** (1935), 201.

‡‡ *Rev. Mod. Phys.* **11** (1939), 36.

§§ *Chem. Rev.* **20** (1937), 99.

apply the technique described in the preceding section to calculate the reaction rate. The only calculations of chemical reaction rates which have been carried out have been of a statistical character such as the transition state method (Chap. VIII, § 8.4). For an account of these theories and their results the reader is referred to *The Theory of Rate Processes*, by Glasstone, Laidler, and Eyring.

XIII

NUCLEAR COLLISIONS

SINCE the first edition of this book was written there has been a great advance in nuclear physics. The availability of strong sources of neutrons and of radioisotopes from the controlled operation of chain reactions in piles will undoubtedly lead to even more rapid progress in the near future. It is not our intention in this chapter to present a comprehensive survey of the information on nuclear collisions available at the time of writing, but rather to illustrate the main aspects of the application of the theory developed in previous chapters (particularly Chapters II, III, and VIII) to these phenomena.

A convenient classification of nuclear collisions is to distinguish those which may be treated by the one-body approximation from those which can only be interpreted by means of the many-body method of the collision complex (Chap. VIII, § 8). The latter include all collisions except those between very light nuclei. Special interest attaches, however, to the study of the impacts of the lightest nuclei, particularly neutrons and protons, for it is largely from such study that we can hope to obtain a detailed knowledge of the fundamental forces between nucleons. Accordingly we first discuss the collisions between the simplest nuclei from this point of view.

Collisions which can be adequately described only in terms of the collision complex or compound nucleus may, in turn, be distinguished by the extent to which they involve resonance phenomena. The behaviour of slow neutrons in nuclear collisions reveals such effects most clearly for the medium and heavy nuclei; whereas protons and α -particles have so far been the most effective projectiles for investigating resonance in light nuclei. Section 2 is devoted to a discussion of these effects.

Resonance phenomena in collisions with medium and heavy nuclei by no means exhaust the range of slow neutron physics. The collisions of slow neutrons with bound protons, their diffraction by crystals, and their polarization by scattering from a ferromagnet (due to the magnetic interaction with the atomic electrons) are all phenomena of great importance and are discussed in §§ 3 and 4.

Collisions of fast particles with medium and heavy nuclei exemplify cases in which the resonance levels of the complex overlap (Chap. VIII, § 8.3) and are briefly discussed in § 5.

Nuclear fission is discussed in the final § 6 as a further example of the

application of the theory to the understanding of nuclear collisions and the identification of reactions arising from different isotopic constituents.

1. The simplest nuclear collisions and the law of force between nucleons

1.1. *The elastic collisions of neutrons and protons*

The simplest collision phenomena involving nucleons are those between a neutron and a proton and between two protons. They may be discussed essentially as one-body problems and are of major importance for the determination of the law of force between nucleons.

We consider first the low energy limit of the cross-section for neutron-proton scattering. This will come almost completely from the scattering of neutrons with relative angular momentum equal to zero. We may represent the force effective in scattering these neutrons by a potential well of range a and depth $k_0^2 \hbar^2 / M$, where M is the neutron mass. From experiment it has been shown that, in the relative coordinate system, the angular distribution of the scattering of neutrons with energies up to 7 M.e.V. or more is still isotropic, and hence must involve only neutrons with $l = 0$. Since the reduced wave-length $\lambda/2\pi$ of the relative motion of a 7 M.e.V. neutron and a proton is 3×10^{-13} cm., it follows that the range cannot be much greater than this. Assuming, as would seem reasonable, that the same potential well is responsible for the binding energy E_0 of the deuteron, the depth constant k_0 of the well may be determined from the relation

$$\tan\{(k_0^2 - \kappa^2)^{1/2} a\} = -(k_0^2 - \kappa^2)^{1/2} / \kappa, \quad (1)$$

where $\kappa^2 = ME_0/\hbar^2$. It is then found that k_0 must be large compared with κ . We may therefore apply formula (33) of Chapter II to give for the low energy cross-section

$$Q \simeq 4\pi(1 + \kappa a)/(k^2 + \kappa^2), \quad (2)$$

where k is the wave number of the relative motion. Ignoring κa compared with unity, this formula gives for the low velocity limit of the cross-section a value of 2.4×10^{-24} cm.², whereas the observed value† is about 21×10^{-24} cm.² Only a small part of this discrepancy can be attributed to neglect of κa , which cannot be much greater than unity.

In order to remove this discrepancy it was suggested by Wigner that

† Hanstein, *Phys. Rev.* **59** (1941), 489; Marshall, *ibid.* **70** (1946), 107; Havens, Rainwater, and Wu, *Bull. Am. Phys. Soc.* **23** (1948), 7; McDaniel and Jones, quoted by Blatt, *Phys. Rev.* **74** (1948), 92.

the depth of the well depends on the total spin. As the ground state of the deuteron is a triplet we would then have, ignoring the finite range,

$$Q = 4\pi \left[\frac{3}{4} \frac{1}{k^2 + \kappa^2} + \frac{1}{4} \frac{1}{k^2 + \mu^2} \right], \quad (3)$$

where $\mu^2 = ME_1/\hbar^2$, E_1 being the magnitude of the binding energy of the singlet state. To fit the experimental cross-section as k tends to zero, E_1 must be taken equal to 50,000 e.V. It is not possible to decide, however, from the scattering data, whether the level is real or virtual. This may be done from a study of the scattering of slow neutrons by molecular hydrogen (§ 3.22) and it is found to be virtual. The depth of the potential well for the singlet state can now be determined.

These considerations remain valid no matter what the detailed form of the interaction may be. It is sufficient that the range be short and the binding energy small compared with the depth. If the interaction is written

$$V = Cf(r/a), \quad (4)$$

involving two parameters C and a , the known binding energies of the two-body system in the 3S and 1S states determine the relation between C and a for a given functional form $f(r/a)$.

To obtain information about the interaction in states with non-vanishing angular momentum it is necessary to observe the scattering of neutrons of reduced wave-length shorter than the range of the interaction. Very considerable interest is attached to this problem for the following reasons.

The binding energy of heavy nuclei is known to be approximately proportional to the number A of nuclear particles. If the interaction between these particles were represented by a formula such as (4), independent of their relative angular momenta, the binding energy would increase as A^2 . This conclusion would be avoided if the function $f(r/a)$ became repulsive at short distances or if repulsive many-body forces occur. As an alternative to these complicated explanations Heisenberg† suggested that the interaction energy should contain as factor an operator H which interchanges the positions and spins of the two particles. Majorana‡ then showed that a further operator M , which exchanges position coordinates only, must be introduced in order that the binding energy per particle should increase up to He^4 and not decline after H^2 .

The simplest interaction of this 'exchange' type is then

$$[(1-g)M + gH]V(r). \quad (5)$$

† *Zeits. f. Physik*, **77** (1932), 1.

‡ *Ibid.* **82** (1933), 137.

g is here a parameter. With this form the interaction is equal in strength for all states of given multiplicity, but is of opposite sign for states of odd and even angular momentum. For singlet states the interaction is $(1-2g)$ times as great as for triplet states, so the value of g may be chosen to give agreement with the virtual binding energy of the 1S state of the deuteron.

By contrast we may take an 'ordinary' interaction

$$[(1-g)1+gMH]V(r). \quad (6)$$

While this gives the same ratio, $(1-2g)$, as (5) for the interaction in corresponding singlet and triplet states, the interaction remains the same in sign as well as magnitude for all states of given multiplicity. This would lead to the so-called absence of saturation for heavy nuclei, i.e. to the proportionality of binding energy to A^2 .

A choice between a predominantly exchange type interaction (5) and an ordinary one such as (6) can be made if the sign of the phase shifts for the p -wave ($l = 1$) can be determined. With the ordinary force of type (6), these phases will be positive; but with the exchange force (5) they are negative. Observation of the sense of the first departure from isotropy of the angular distribution in relative coordinates would enable the choice to be made. The energy at which this deviation first reaches a certain magnitude will be somewhat greater with exchange type forces because, with a repulsive potential, the p -phases increase less rapidly initially than with an attractive potential. As the range of the forces can be estimated from the binding energies of the triton and from proton-proton scattering, the extent of the departure from isotropy can be estimated for both types of force.† Fig. 57 illustrates the angular distributions, in relative coordinates, for 13.8 and 20.8 M.e.V. neutrons, calculated on the assumption of two forms of the function $f(r/a)$ with the alternative 'ordinary' and 'exchange' operators.

As the neutron energy increases still further, the influence of higher angular momenta becomes important and the distinction between exchange and ordinary forces is no longer so clear. Fig. 58 illustrates the behaviour of the ratio $I(\pi)/I(\frac{1}{2}\pi)$ of the intensity scattered at 180° to that at 90° as a function of neutron energy for the same forces as are assumed in Fig. 57.

At sufficiently high energies for Born's approximation to be valid there is again a clear distinction between the predictions for the two

† Buckingham and Massey, *Proc. Roy. Soc. A*, **163** (1937), 281; Ramsey, *Proc. Roy. Soc. A*, **191** (1947), 195; Blatt, *Phys. Rev.* **74** (1948), 92.

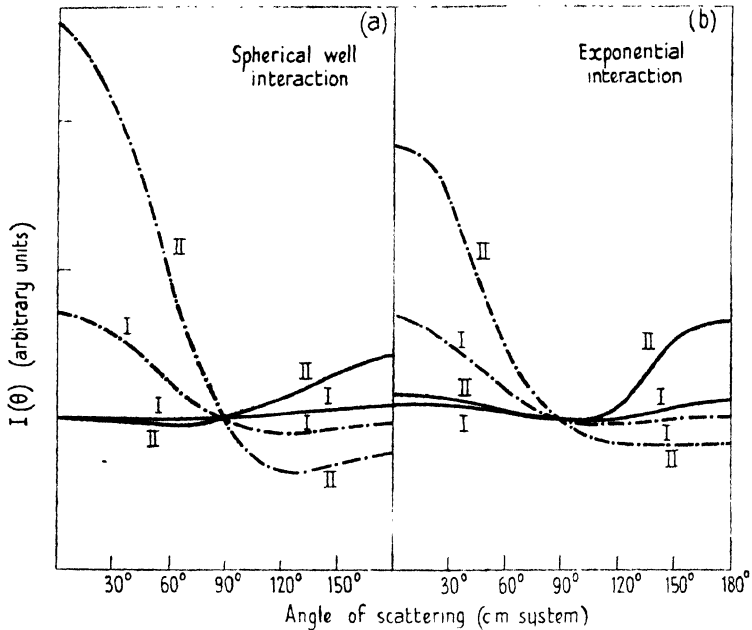


FIG. 57. Theoretical angular distributions in the centre of mass system for scattering of neutrons by protons. Curves I, II refer to 13.3 and 20.8 M.e.v. neutrons respectively. The scale has been adjusted so that $I(\frac{1}{2}\pi) = 1$ in all cases.

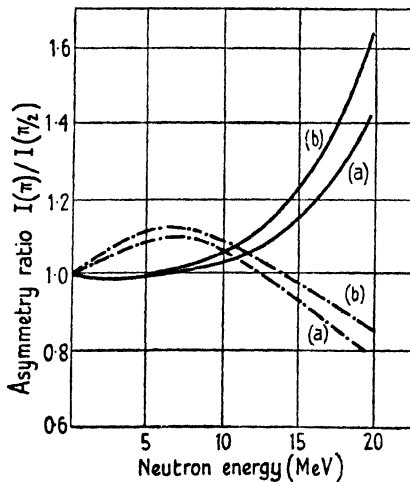


FIG. 58. Theoretical asymmetry ratio $I(\pi)/I(\frac{1}{2}\pi)$ for the scattering of neutrons by protons assuming different laws of force.

———— assuming exchange forces.

- - - - - assuming ordinary forces.

(a) Spherical well interaction

(b) Exponential interaction

$V(r) = -17$ M.e.v. ($a < 2.8 \times 10^{-13}$ cm.)
 $= 0$ ($a > 2.8 \times 10^{-13}$ cm.)

$V(r) = -C \exp(-2r/a)$,
 $C = 122$ M.e.v. ($a = 1.73 \times 10^{-13}$ cm.)

types of force. The differential cross-section is given, according to eq. (5) of Chapter VII, by

$$I(\theta) = \frac{4\pi^2 M^2}{\hbar^4} \left| \int e^{i\mathbf{k}\mathbf{n}_0 \cdot \mathbf{r}'} V(r') e^{\mp i\mathbf{k}\mathbf{n} \cdot \mathbf{r}'} d\tau' \right|^2 \frac{1}{4} \{3 + (1 - 2g)^2\}, \quad (7)$$

where $\mathbf{n}_0 \cdot \mathbf{n} = \cos \theta$.

With ordinary forces the negative sign is to be taken in the second exponent, whereas the effect of the exchange operators is to reverse this sign. The maximum value of $I(\theta)$ will occur when $|\mathbf{k}\mathbf{n}_0 \mp \mathbf{k}\mathbf{n}|$ is small for the respective cases, or, in terms of the angle θ , at small θ with ordinary forces, for $\theta \simeq \pi$ with exchange forces. The struck protons will be mainly projected at nearly 90° to the direction of the incident neutrons in the former case and in the direction of incidence in the latter. The effect is very similar to charge exchange in the collision of an ion with a neutral atom of the same kind (Chap. XII, § 3.4). Fig. 59 illustrates the effect for 83 M.e.V. neutrons and the same interactions as in Figs. 57 and 58.

It is, of course, clear that there exist many other possibilities as far as the combination of exchange and other operators is concerned. The operator combinations which occur in the meson theories have been studied,[†] as also the effect of non-central interactions[‡] of the type required by the existence of the quadrupole moment of the deuteron. Although these various possibilities give results which differ in detail, it is still possible to distinguish the forces as predominantly of ordinary or exchange type, affecting the scattering, at least qualitatively, in the ways described above.

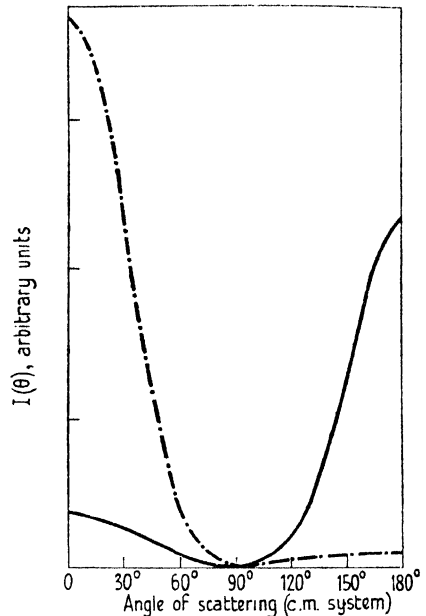


FIG. 59. Theoretical angular distribution in the centre of mass system for scattering of 83 M.e.V. neutrons by protons, assuming the spherical well interaction as in Fig. 57(a).

— assuming exchange forces.
 - · - · assuming ordinary forces.

[†] Hulthén, *Arkiv. för Mat., Ast. o. Fys.* **29** (1943), 1; **30** (1943), 1; **31** (1944), 1; Ramsey, *Proc. Roy. Soc. A*, **191** (1947), 195.

[‡] Rarita and Schwinger, *Phys. Rev.* **59** (1941), 436; *ibid.* 556; Hepner and Peierls, *Proc. Roy. Soc. A*, **181** (1943), 43; Hu and Massey, *Nature* **160** (1947), 794.

At the time of writing the experimental evidence derived from the scattering of neutrons of a few M.e.V. energy has failed to provide decisive evidence for or against the exchange character of the fundamental nuclear interaction. Recently,[†] however, investigations have been made of the projection of protons by 100 M.e.V. neutrons stripped from 200 M.e.V. deuterons generated by the 184 inch cyclotron at Berkeley. Although detailed interpretation of the results is difficult,[‡] it is already clear that more protons are projected in the direction of incidence of the neutrons than would be so if the interaction were of the ordinary force type (6).

1.2. *The scattering of protons by protons*

The measurement of the intensity of scattering of protons by protons can be carried out with greater precision than that of neutron-proton scattering. It has the disadvantage of yielding information only on the interaction in states which are antisymmetric with respect to interchange of the particles.

According to the discussion in Chap. V, § 5, the effective cross-section for the scattering of protons of velocity v through an angle θ by stationary protons is given by

$$I(\Theta) d\omega = \{3|f(2\Theta) - f(\pi - 2\Theta)|^2 + |f(2\Theta) + f(\pi + 2\Theta)|^2\} \cos \Theta d\omega, \quad (8)$$

where
$$f(\theta) = \frac{1}{2ik} \sum (2n+1)(e^{2i\eta_n} - 1)P_n(\cos \theta).$$

η_n is such that, if $V_n(r) + \epsilon^2/r$ is the interaction between protons with n units of angular momentum, the asymptotic form of the proper solution of the equation

$$\frac{d^2 G_n}{dr^2} + \left[k^2 - \frac{4\pi^2 M}{\hbar^2} V_n(r) - \frac{\epsilon^2}{r} - \frac{n(n+1)}{r^2} \right] G_n = 0, \quad (9)$$

is
$$\sin(kr - \alpha \log 2kr - \frac{1}{2}n\pi + \eta_n), \quad (10)$$

where $k = \pi Mv/\hbar$, $\alpha = \epsilon^2/\hbar v$, M being the mass of a proton.

We may write
$$\eta_n = \zeta_n + \kappa_n, \quad (11)$$

where $\zeta_n (= \arg \Gamma(1 + i\alpha + n))$ is the phase shift which would be produced in the absence of the potential $V_n(r)$, so that

$$f(\theta) = f_c(\theta) + \frac{1}{2ik} \sum e^{2i\zeta_n} (e^{2i\kappa_n} - 1) (2n+1) P_n(\cos \theta). \quad (12)$$

[†] Hadley, Kelly, Leith, Segrè, Wiegand, and York, *Phys. Rev.* **72** (1948), 1114.

[‡] For references see footnote p. 349.

$f_c(\theta)$ is the value obtained for the scattering by the Coulomb repulsion alone, viz.

$$f_c(\theta) = \frac{\epsilon^2}{Mv^2} \operatorname{cosec}^2 \frac{1}{2}\theta \exp[-i\alpha \log 2 \sin^2 \frac{1}{2}\theta + 2i\zeta_0 + i\pi]. \quad (13)$$

Using (12) and (13), the ratio R of the scattering to that by the Coulomb field alone may be expressed in terms of the phases κ_n . For low energy protons only κ_0 will be important. In that case

$$R = 1 + I_a/I_c, \quad (14)$$

where I_c , the contribution from the Coulomb field, is given by

$$I_c = \frac{4\epsilon^4}{M^2v^4} \{\operatorname{cosec}^4\Theta + \sec^4\Theta - \cos(\alpha \log \tan^2\Theta) \operatorname{cosec}^2\Theta \sec^2\Theta\}, \quad (15)$$

and I_a , the anomalous scattering, by

$$I_a = \frac{8\epsilon^4}{M^2v^4} \left[\frac{2 \sin^2 \kappa_0}{\alpha^2} - \frac{\sin \kappa_0}{\alpha} \{\operatorname{cosec}^2\Theta \cos(\alpha \log 2 \sin^2 \Theta + \kappa_0) + \sec^2\Theta \cos(\alpha \log 2 \cos^2 \Theta + \kappa_0)\} \right]. \quad (16)$$

In particular, at an angle of 45° ,

$$R = 1 - \frac{\sin 2\kappa_0}{\alpha} + \frac{\sin^2 \kappa_0}{\alpha^2}.$$

The anomalous scattering of protons by protons was first observed by White,[†] and by Tuve, Heydenburg, and Hafstad.[‡] This early work indicated the existence of a short-range attraction. This was confirmed by the extensive measurements of Herb, Kerst, Parkinson, and Plain[§] which were analysed in detail by Breit, Thaxton, and Eisenbud.^{||} The experiments covered an energy range from 860 to 2,392 k.e.V. and an angular range from 30° to 90° in the centre of mass system. At each energy a single-phase parameter κ_0 could be found which, on substitution in (16), gave a good representation of the observed scattering over the angular range covered. The parameter was positive, showing the anomalous force to be attractive. As no higher-order phases such as κ_1 were required to fit the observations it is clear that the force, like that between neutron and proton, is of short range.

Breit, Thaxton, and Eisenbud^{††} assumed that the anomalous interaction could be written in the form (4) and, taking definite forms for the 'shape' function $f(r/a)$, attempted to derive information about the

[†] *Phys. Rev.* **49** (1936), 309.

[‡] *Ibid.* p. 432.

[§] *Ibid.* **55** (1939), 998.

^{||} *Ibid.* p. 1018.

^{††} *Loc. cit.* See also Hoisington, Share, and Breit, *Phys. Rev.* **56** (1939), 884.

details of the interaction from the derived phases κ_0 . They found that, for the shapes assumed, the range could be chosen to reproduce approximately the variation of κ_0 with energy. The important result emerged that, for the same assumed shape of interaction, the anomalous proton-proton force is very nearly equal in strength to the force between a neutron and proton in a 1S state.

Recent work,† which has extended the energy range up to 14.5 M.e.v., has confirmed these results. Fig. 60 illustrates the comparison of the

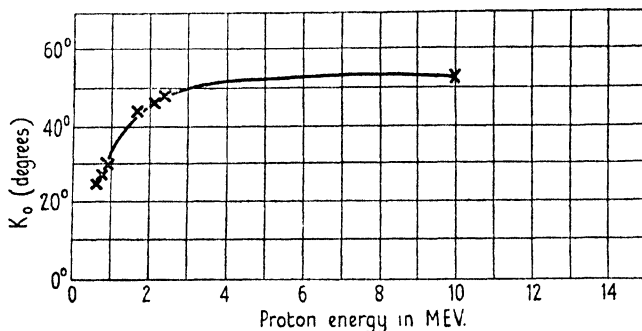


FIG. 60. Comparison of phase angle κ_0 derived from observations of proton-proton scattering (indicated by x) with that calculated (full line curve) on the assumption of an anomalous interaction:

$$\begin{aligned}
 V(r) &= -C \quad (r < a) \\
 &= 0 \quad (r > a),
 \end{aligned}$$

with $C = 10.5$ M.e.v. and $a = 2.8 \times 10^{-13}$ cm.

phase κ_0 , given by taking the anomalous proton-proton interaction to be of spherical well form with suitable range and depth, with that derived from the experimental results.

There is still doubt as to how close the anomalous interaction between two protons in an S state approaches the 1S neutron-proton interaction, but the agreement is certainly good. At the time of writing there is no definite evidence of any contribution from phases of higher order. Just as for neutron-proton collisions the determination of the

† (Experimental): Heydenburg, Hafstad, and Tuve, *Phys. Rev.* **56** (1939), 1078; Ragan, Kanne, and Taschek, *ibid.* **60** (1941), 628; May and Powell, *Proc. Roy. Soc. A*, **90** (1947), 170; Wilson, *Phys. Rev.* **71** (1947), 384; Wilson and Creutz, *ibid.* p. 339; Wilson, Lofgren, Richardson, Wright, and Shankland, *ibid.* p. 560; Dearnley, Oxley, and Perry, *ibid.* **73** (1948), 1290; Blair, Freier, Lampi, Sleator, and Williams, *ibid.* **74** (1948), 553. (Theoretical): Thaxton and Hoisington, *ibid.* **56** (1939), 1194; Breit, Kittel, and Thaxton, *ibid.* **57** (1940), 255; Peierls and Preston, *ibid.* **72** (1947), 250; Foldy, *ibid.* p. 731; Ramsey, *Proc. Roy. Soc. A*, **194** (1948), 228; Breit, Broyles, and Hall, *Phys. Rev.* **73** (1948), 869.

sign of the κ_1 phase is important, because it will depend on whether the interaction is of exchange type or not.

1.3. *The elastic scattering of neutrons and protons by deuterons*

The only other elastic scattering problems involving nucleons which are amenable to detailed calculation are those in which neutrons or protons interact with deuterons. Even in this case the problem is complex and the accuracy of the results rather difficult to estimate. The most extensive calculations have been carried out by Buckingham and Massey.† They assumed the fundamental interaction between nuclei to be given by a potential function

$$V(r) = -Ce^{-2r/a},$$

with $C = 242 mc^2$, $a = 1.73 \times 10^{-13}$ cm. (as illustrated in Figs. 57, 58), associated either with an operator of ordinary or exchange type. This function gives good agreement‡ with the binding energy of H^3 . With these interactions they solved the scattering problem to the same approximation as that used by Morse and Allis for the scattering of slow electrons by helium allowing for exchange (Chap. X, § 6). Good agreement with the observed§ intensity and angular distribution of scattered protons with 1.85 M.e.V. incident energy was found,|| particularly if the interaction is taken to be of exchange type. At these energies the anomalous (non-Coulomb) scattering is large and involves both κ_0 and κ_1 phases. For neutrons with energies ranging from thermal to 7 M.e.V. the agreement with the observed total cross-section†† is also quite good when exchange forces are assumed, particularly in view of the experimental uncertainties.

The chief doubt as to the accuracy of the theory concerns the importance of polarization effects arising from the distortion of the deuteron by the incident particle. As the wave function $\Psi(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_1 - \mathbf{r}_3)$ used to describe the scattering has the correct symmetry in the coordinates $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ of the three particles, it does include some contributions from functions $\phi(\mathbf{r}_1 - \mathbf{r}_2)$ which represent states of a deuteron other than the ground state. The importance of terms not included in this way is not yet clear.

† *Proc. Roy. Soc. A*, **179** (1941), 123; *Phys. Rev.* **71** (1947), 558; *ibid.* **73** (1948), 260. For scattering at high energies see Wu and Ashkin, *Phys. Rev.* **73** (1948), 986; Chew, *ibid.* **74** (1948), 809.

‡ Present and Rarita, *ibid.* **51** (1937), 788.

§ Sherr, Blair, Kratz, Bailey, and Taschek, *ibid.* **72** (1947), 662.

|| Buckingham and Massey, *loc. cit.*; Critchfield, *Phys. Rev.* **73** (1948), 1.

†† Aoki, *Proc. Phys. Math. Soc. Japan*, **21** (1939), 232; Ageno, Amaldi, Bocciarelli, and Trabacchi, *Il Nuov. Cimento*, **9** (1943), 1; *Phys. Rev.* **71** (1947), 20; Nuckolls, Bailey, Bennett, Bergstrahl, Richards, and Williams, *ibid.* **70** (1946), 805.

2. Many-body resonance phenomena in nuclear collisions

We now consider phenomena in which the one-body approximation is no longer valid. This is so for collisions of all but the lightest nuclei. For such cases the method of the collision complex, or compound nucleus, must be used. In Chapter VIII we have distinguished two important cases, those in which the level spacing in the complex is greater than the level widths and those in which the levels overlap. It is only in the former case that resonance effects can be expected. From their study it is possible, not only to establish the correctness of the theoretical interpretation, but also to obtain valuable information about the energy-level systems of highly excited nuclei and the relative importance of processes contributing to the level widths. Less detailed information is forthcoming from the cases in which the levels overlap.

We shall first discuss certain resonance reactions to illustrate the various possibilities and results obtained. Resonance phenomena associated with medium and heavy nuclei have been studied almost exclusively by use of slow neutrons as bombarding particles. In these nuclei the level spacing is much closer for a given energy of excitation than for light nuclei (see § 2.1). It is therefore necessary to keep the excitation as low as possible in order that the spacing should remain larger than the level widths. This limits us to slow particles. Charged particles are therefore excluded because of their inability to penetrate the high potential barrier.

On the other hand, resonance effects in light nuclei have usually been studied using charged particles. The reason for this is that the level spacings are relatively much greater (see § 2.1), so that neutrons with energies of the order of 10^8 to 10^9 e.V. are required. Neutron sources with controllable energy in this range are only now becoming readily available, whereas sources of charged particles, such as protons and α -particles, with energies covering this range have been available for some years. For light nuclei the Coulomb potential barrier is low enough to allow the entry of such particles. Up to the present the main information on resonance in light nuclei has come from the study of disintegration by α -particles, radiative capture of protons, and elastic scattering of α -particles and of protons. The information is less detailed than that provided from the investigations of slow neutrons.

In interpreting resonance phenomena the 'one-level' formula of Chapter VIII (130) for a rearrangement collision and (132) for elastic scattering are assumed. If it is necessary to include the effect of more than one resonance level the number of unknown constants is, in most

cases, so considerable as to render the formulae useless. It does, however, appear that for many reactions the one-level formula is adequate. Although in discussing the method of the collision complex in Chap. VIII, § 8, we made no explicit mention of the possibility of electromagnetic radiation, it is clear that it may be taken into account by introducing an appropriate partial level width Γ_r , as will be done in the discussion below.

2.1. Theoretical level spacing in compound nuclei

Although it is beyond the scope of this book to discuss in detail the way in which theoretical estimates of level spacings in compound nuclei have been derived, we summarize here the main results obtained. They provide a qualitative description of the level distribution.

For the light nuclei the best theoretical model seems to be the free particle model† as modified by Bardeen‡ to allow for exchange forces. The nucleus is treated as a mixture of two gases, of neutrons and protons respectively, obeying the Fermi-Dirac statistics and confined within a potential box. With exchange forces the effective depth of this box depends on the wave number of the particle concerned,§ and this is the effect allowed for by Bardeen. Applying the methods of statistical mechanics in the usual way the level spacing comes out to be

$$D = 3 \times 10^6 x^4 e^{-x} \text{ e.V.}, \quad (17)$$

where, in terms of the mass number A and excitation energy U in M.e.V.,

$$x = (AU/4 \cdot 36)^{\dagger} \quad (18)$$

and the nuclear radius R has been taken as $1 \cdot 48 A^{1/3} \times 10^{-13}$ cm.||

For medium and heavy nuclei the best approximation is probably the liquid drop model suggested by Bohr and Kalckar.†† If the contribution from dilatational waves is ignored and the same nuclear radius taken as for (18),‡‡ it is found that

$$D = 6 \cdot 1 \times 10^6 A^{-1/7} U^{5/6} \exp\{-0 \cdot 65 A^{2/7} U^{4/7}\} \text{ e.V.} \quad (19)$$

Table I gives some typical values according to each formula.

† Bethe, *Phys. Rev.* **50** (1936), 336, and *Rev. Mod. Phys.* **9** (1937), 79; Oppenheimer and Serber, *Phys. Rev.* **50** (1936), 391; see also Margenau, *ibid.* **59** (1941), 627.

‡ *Ibid.* **51** (1937), 799.

§ van Vleck, *ibid.* **48** (1935), 367.

|| Derived from the radii of radioactive nuclei. x is proportional to the nuclear radius.

†† See Bethe, *Rev. Mod. Phys.* **9** (1937), 79.

‡‡ In (19) the exponent is proportional to the 6/7th power of the nuclear radius, the outside factor to the $-3/7$ th power.

TABLE I

Mass number	Level spacing (in e.V.) for different excitation energies								Typical excitation energies (M.e.V.) from capture of		
	(a) According to formula (17)								Slow neutrons	α -particles of 2 M.e.V.	Deuterons of 2 M.e.V.
	U = 5 M.e.V.		U = 10 M.e.V.		U = 15 M.e.V.		U = 20 M.e.V.				
(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)				
10	—	4.6×10^8	—	1.4×10^8	—	5.1×10^8	7.3×10^8	2.4×10^8	9.3	11	18
20	—	2.2×10^8	7.3×10^8	4.9×10^8	3.6×10^8	1.1×10^8	1.7×10^8	4.2×10^8	9.5	12	19
50	—	5.6×10^8	8.7×10^8	7.1×10^8	1.8×10^8	1.2×10^8	4.2×10^8	2.6×10^8	9.1
100	8.7×10^8	1.6×10^8	4.3×10^8	1.1×10^8	3×10^8	1.3×10^8	320	18	8.2
200	4.2×10^8	3.5×10^8	320	128	6	8.2	0.17	0.7	6.9

It will be seen from comparison with the level spacings deduced from experiment (see §§ 2.22, 2.34) that the theoretical spacings are too large. The sensitiveness of either theoretical expression to the numerical value of the exponent involved is such that good agreement could hardly be expected. On the other hand, both formulae contain the important feature that the spacing decreases exponentially as the mass number A and excitation energy U increase.

2.2. Resonance phenomena in medium and heavy nuclei involving slow neutrons

The experimental researches, from which slow neutron physics has developed, have been mainly concerned with the behaviour of neutrons with energies ranging from a fraction of an electron volt to some hundreds of electron volts or so. Such neutrons have insufficient energy to excite a nucleus in an inelastic collision and possess wave-lengths considerably greater than nuclear dimensions (the wave-length of a neutron with energy V e.V. is $2.6 \times 10^{-9} V^{-\frac{1}{2}}$ cm.). As a result the possibilities are limited to an extent which assists theoretical interpretation and prediction.

Following the method of the collision complex we regard the collision of a slow neutron with a nucleus as first producing a complex, the compound nucleus, which breaks up again with release of the surplus energy. There are five ways in which the break up can occur:

- (a) The neutron may be re-emitted with its original energy. In this case the collision will be an elastic one.
- (b) Gamma radiation may be emitted, the collision being then one of radiative capture.
- (c) An α -particle may be emitted.
- (d) A proton may be emitted.
- (e) The complex may divide into comparable fragments, i.e. nuclear fission may take place.

For energetic reasons nuclear fission due to slow neutrons is confined to impacts with a limited number of heavy nuclei. Some further discussion of fission will be given in § 6. It is also for energetic reasons that the emission of protons or α -particles is confined to a limited number of processes involving light nuclei. In general, then, a slow neutron impact results in either elastic scattering of the neutron or its capture accompanied by emission of radiation. We shall therefore confine ourselves in the first instance to collisions of this type.

2.21. *Application of the one-level formula.* If we suppose that the principal effects in slow neutron collisions arise from a single resonance level of the compound nucleus, we may apply formula (135) of § 8.1, Chap. VIII, to give, for the capture cross-section

$$Q_c = \frac{\pi}{2k^2} \left(1 \pm \frac{1}{2s+1} \right) \frac{\Gamma_r \Gamma_n}{(E - E_R)^2 + \frac{1}{4}(\Gamma_r + \Gamma_n)^2}. \quad (20)$$

The only way the compound nucleus can break up is by re-emission of a neutron with its initial energy or by emission of radiation. Γ_n , Γ_r are the corresponding partial level widths, E_R is the resonance energy, E the neutron energy, and k its wave number. The factor $\frac{1}{2}\{1 \pm 1/(2s+1)\}$ arises if the struck nucleus has s units of spin, the \pm sign depending on whether the angular momentum quantum number of the resonance level of the complex is $s \pm \frac{1}{2}$.

We find similarly for the elastic scattering

$$Q_{el} = \frac{1}{2} \frac{\pi}{k^2} \left(\left| \left(1 \pm \frac{1}{2s+1} \right) - 2ikR + \frac{\Gamma_n}{E_R - E - \frac{1}{2}i(\Gamma_r + \Gamma_n)} \right|^2 + \left(1 \mp \frac{1}{2s+1} \right) |2ikR|^2 \right), \quad (21)$$

the upper signs being taken when the angular momentum quantum number of the resonance level is $s + \frac{1}{2}$, the lower when it is $s - \frac{1}{2}$. In deriving this result it is assumed that kR is small, R being the nuclear radius.

We first note certain general features of these formulae. For neutron energies near E_R the variation of Q_c with energy will be of the typical resonance type, being sharper the smaller the total width Γ ($= \Gamma_r + \Gamma_n$). There are two other characteristic types of energy variation which arise under certain conditions. It was shown in § 8.22, Chap. VIII, that Γ_n is at first proportional to the neutron velocity v . Hence for low velocities Q_c will vary like v^{-1} , provided the denominator of (20) varies only slightly with E . This will be the case if either E_R or Γ is much greater than E ,

a condition which, as we shall see, is most easily satisfied for light nuclei which have broad levels widely spaced.

The remaining possibility is that the resonance energy be negative. In that case Q_c will show a monotonic decrease with increasing neutron energy, first as E^{-1} and finally as $E^{-5/2}$.

When the conditions are such that the capture cross-section is varying as E^{-1} , the scattering cross-section will be independent of E as both terms inside the brackets in (21) will vary as E . Under these conditions the total cross-section will be of the form $g_c E^{-1} + g_s$, where the first term results from radiative capture, the second from elastic scattering, g_c and g_s being constants.

The capture cross-section is determined, when the spin factor $\{1 \pm 1/(2s+1)\}$ is known, by the resonance energy E_R and the partial widths Γ_n , Γ_r . Writing

$$\Gamma_n = \Gamma_n^R \left(\frac{E}{E_R} \right)^{\frac{1}{2}}, \quad (22)$$

where Γ_n^R is the neutron width at resonance, we have for the cross-section Q_c^{\max} at exact resonance,

$$Q_c^{\max} = \frac{h^2}{4\pi m E_R} \frac{\Gamma_r \Gamma_n^R}{(\Gamma_n^R + \Gamma_r)^2} \left(1 \pm \frac{1}{2s+1} \right). \quad (23)$$

The ratio $\Gamma_r \Gamma_n^R / (\Gamma_n^R + \Gamma_r)^2$ may therefore be determined from observations of Q_c^{\max} and E_R . It is also possible, by observing the variation of Q_c with E , to measure $\Gamma_r + \Gamma_n^R$ directly from the width of the resonance. This gives the values of the sum and of the product of Γ_r and Γ_n^R , so that the pair of values which the partial widths must have is determined except for the decision as to which is the larger. To decide this, recourse must be had to observation of elastic scattering. The resonance contribution to this cross-section is $Q_c \Gamma_n^R / \Gamma_r$, where Q_c is the capture cross-section, and will be greater or smaller than Q_c according as the neutron or radiation width is the greater. Except for light elements Γ_r is found to be much larger than Γ_n^R .

In most cases the spin factor is not known and ambiguity is introduced by the presence of more than one isotope in the absorbing material. Furthermore, in analysing experimental results care must be taken that the observed resonance is not largely due to so-called 'Doppler' broadening—the effect of the thermal motion of the struck nuclei. This contributes† an apparent level width Δ , where

$$\Delta = 2(m E_R \kappa T / M)^{\frac{1}{2}},$$

† Bethe, *Rev. Mod. Phys.* 9 (1937), 140.

m being the mass of a neutron, M of a nucleus, T the temperature of the material containing the nuclei concerned, and κ is Boltzmann's constant.

2.22. Experimental results. In recent years there have been considerable advances in technique which have made practicable much more detailed studies of slow neutron cross-sections. We shall content ourselves here with choosing illustrations from this recent work. For the earlier work, which often involved use of indirect methods, the reader is referred to H. Bethe, *Reviews of Modern Physics*, 9 (1937), Chap. X.

The availability of strong neutron sources from fission piles has made it possible to obtain monochromatic beams of slow neutrons by Bragg reflexion at a suitable angle from a crystal such as LiF. With these beams available the observations required for the analysis given above may be obtained.

A further method which has proved very useful is that of the modulated neutron source first introduced by Alvarez† and by Fertel, Gibbs, Moon, Thomson, and Wynn-Williams.‡ By means of a discriminating amplifier or similar device it is possible to select for observation only those neutrons which arrive at the detecting system within a chosen time interval since the last burst of neutrons was released from the source, i.e. to select neutrons with a given velocity range. This method enables the resonance energies to be determined and also the product $Q_c^{\max}\Gamma^2$, but is not yet of sufficiently high resolution to determine Q_c^{\max} itself. In the region in which Q_c behaves like E^{-1} the method may be used to determine q_c and g_s .

One of the most important elements from the point of view of neutron absorption is cadmium. This is because it strongly absorbs neutrons of ordinary thermal energy. Information about the constants of the excited complex formed on capture of a slow neutron by cadmium is more definite than for any other element.

Fig. 61 illustrates the variation with energy of the total cross-section of cadmium obtained by Sawyer, Wollan, Bernstein, and Peterson§

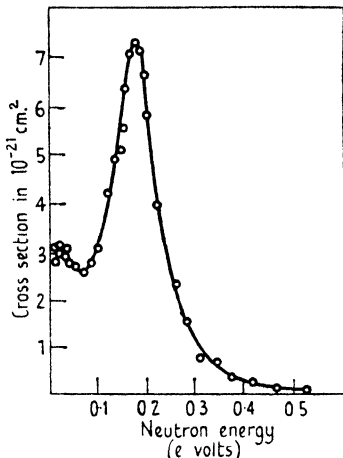


FIG. 61. Observed total absorption cross-section of cadmium towards slow neutrons.

† *Phys. Rev.* **54** (1938), 609.

‡ *Proc. Roy. Soc. A*, **175** (1940), 316.

§ *Phys. Rev.* **72** (1947), 109.

using neutrons diffracted by crystals. The resonance character of the absorption is clear, and it is found that the cross-section is well represented by the formula (20) with $Q_c^{\max} = 7.25 \times 10^{-21}$ cm.², $E_R = 0.178$ e.V., and $\Gamma = 0.110$ e.V. These values are in very good agreement with those obtained recently by other observers.†

It has been shown by Moyer, Peters, and Schmidt‡ that the isotope responsible for the strong absorption is Cd¹¹³ whose abundance percentage in the natural element is 12.3 per cent. The spin quantum number of this isotope is $\frac{1}{2}$. Dunning, Pegram, Fink, and Mitchell§ showed that the elastic cross-section is not greater than 1 per cent. of the total. Finally, measurements by Berman|| have placed the value of the elastic scattering cross-section as $40 \pm 15 \times 10^{-24}$ cm.²

From these results it is possible to assign the separate values 0.11 and 0.60×10^{-3} e.V. to the partial widths Γ , and Γ_n^R respectively and to decide that the angular momentum quantum number of the resonance level responsible is 1 and not 0.

Data as complete as for cadmium is not available for other elements. Table II summarizes the results of a number of recent measurements for different elements.†† These results are analysed as far as possible, making, if necessary, plausible assumptions as to the isotope responsible and taking the spin factor $\{1 \pm 1/(2s+1)\}$ as unity. It will be noted that europium, dysprosium, and mercury all exhibit a resonance level with small negative energy.

In all cases the compound nucleus formed by neutron capture has an excitation energy of the order $7-9 \times 10^6$ e.V. From the distribution of the resonance energies it is possible to obtain some idea of the level separation for this excitation. A specially interesting case is that of tantalum, which consists of a single isotope only. Five resonance levels have been observed between 0 and 40 e.V., indicating a level spacing of somewhat less than 10 e.V. for a heavy nucleus. A similar spacing is indicated for iodine, which also consists of a single isotope, but there is evidence from the table that the spacing becomes wider for lighter nuclei. Both cobalt and manganese exhibit no resonance level below 100 e.V. and earlier experiments have revealed similar behaviour for copper and arsenic. This would be expected because of the fewer degrees of freedom in the lighter nuclei (see § 2.1).

† Rainwater and Havens, *ibid.* **70** (1946), 136; Rainwater, Havens, Wu, and Dunning, *ibid.* **71** (1947), 65; Zinn, *ibid.* p. 752.

‡ *Ibid.* **69** (1946), 666. § *Ibid.* **48** (1935), 265. || *Ibid.* **72** (1947), 986.

†† For further results see Rainwater, Havens, Dunning, and Wu, *ibid.* **73** (1948), 733 and 963.

TABLE II
Analysis of Experimental Data on Cross-Sections for Slow Neutron Collisions with Nuclei

Element	Resonance energies E/E_0 (e.v.)	Maximum cross-sections $Q_{max} \times 10^{-24}$ cm. ² (These refer to the lowest positive resonance levels)	Radiation width Γ_r (e.v.)	Neutron escape width $\Gamma_n \times 10^{-3}$ (e.v.)	Doppler width Δ (e.v.)	Low velocity limit of cross-section $q_0 E^{-1+g_0}$		Remarks and references When more than one reference is given the data have been taken from the first
						$q_0 \times 10^{-24}$ volt ² cm. ²	$g_0 \times 10^{-11}$ cm. ⁻¹	
Mn	300	2.24	2.3	(c) Resonance cross-section due mainly to elastic scattering (k)
Zr	115	6.4	6.7	(c) Resonance cross-section due mainly to elastic scattering (l)
Cr	1.1, 2.3, 7.6	0.74	6.8	(d)
Rh	1.28	4,000	0.16	0.43	0.04	(e)
Ag	5.1, 16, 45	7,250	0.11	0.60	0.013	9.05	6.6	(e), (f)
Cd	0.178	(g)
In	1.44, 3.6, 8.6	26,000	0.09	1.8 (1.7)	0.036	(d) Resonance cross-section due to Cd ¹¹³ (n) (12.3% abundance). Spin $\frac{1}{2}$, and to $J = 1$ level of complex (m)
Sb	5.8, 15, 21	0.64	4.2	(e) Resonance attributed to In ¹¹⁵ (95.5% abundance)
I	20.6, 32, 42	[80]	[0.45]	[0.4] (6.3)	0.126	1.12	3.8	(c) Constants in [] very rough (j)
Sm	0.036, 10, 33	15,500	0.074	0.34 (0.43)	0.008	(h) Resonance due to Sm ¹⁴⁹ (f) (17% abundance)
Eu	-0.011, 0.465, 3.3 9.2, 22	0.0172	(h) Resonance attributed to either of the two isotopes each of 50% abundance
Gd	0.031	44,000	0.095	0.42 (0.25)	(h) Resonance due to Gd ¹⁵⁷ (j) (17% abundance)
Dy	-1.01	..	0.10	(h)
Ta	4.1, 10, 13, 22, 37	3.0	7.2	(d)
W	4.0, 7.4, 18.0	2.72	5.7	(d)
Os	6.5, 8.8, 20, 28, 42	2.7	15	(d)
Ir	0.63, 1.35, 6.0	[530] [605]	[0.25] [0.36]	[0.11] [0.25]	0.004	6.4	1.4	(e), (f)
Pt	11.5, 18.2	1.0	12	(d)
Au	4.8	(d)
Hg	-2.0	(f)
Tl	0.6	9.7	(e)

(a) Rainwater and Havens, *Phys. Rev.* **70** (1946), 136.
 (b) Rainwater and Havens, *Ibid.* p. 154.
 (c) Rainwater, Havens, Wu, and Dunning, *ibid.* **71** (1947), 65.
 (d) Havens, Wu, Rainwater, and Meaker, *Ibid.* p. 165.
 (e) Wu, Rainwater, and Havens, *Ibid.* p. 174.
 (f) Lapp, van Horn, and Dempster, *Ibid.* p. 745.
 (g) Zinn, *Ibid.* p. 752.
 (h) Sturm, *Ibid.* p. 757.
 (i) Sawyer, Wollan, Bernstein, and Peterson, *ibid.* **72** (1947), 109.
 (j) Jones, *Ibid.* p. 362.
 (k) Burre and Goldhaber, *ibid.* **71** (1947), 141; Seidl, Harris, and Langsdorf, *ibid.* **72** (1947), 108.
 (l) Harris, Langsdorf, and Seidl, *ibid.* p. 866.
 (m) Herman, *Ibid.* p. 986.
 (n) Meyer, Peters, and Schmidt, *ibid.* **69** (1946), 666.
 (o) Hornbostel, Goldsmith, and Manley, *ibid.* **58** (1940), 18.

The radiation width remains close to 0.1 e.V. for most nuclei. According to the theory, the true neutron width should be roughly proportional to $E_R^{\frac{1}{2}}$ for neighbouring nuclei. Using the cadmium result to fix the constants, we have

$$\Gamma_n^R = 1.4 E_R^{\frac{1}{2}} \times 10^{-3} \text{ e.V.}, \quad (24)$$

with E_R measured in e.V. The experimental values for the neighbouring elements are hardly accurate enough, and the analysis not sufficiently unambiguous, to check the general validity of this expression, but it is certainly not in definite disagreement with observation. This may be seen from the fifth column of Table II in which the values given from (24) (enclosed in round brackets) are compared with those derived from experiment. There seems also to be evidence from iridium that the constant in (24) decreases for the heavier nuclei, as would be expected (see Chap. VIII (8.31)).

On the other hand, the neutron level width should be much greater for the lighter elements, partly because of the higher energy of the resonance levels and partly because of the fewer degrees of freedom among which the excitation energy is shared. This increases the chance of sufficient energy concentrating on a single particle to enable it to escape from the complex. Confirmation is provided by the experimental proof that for cobalt† and manganese‡ the resonance is associated mainly with elastic scattering and not radiative capture.

According to the one-level formula the cross-section for capture in the limit of low velocities, $q_c E^{-\frac{1}{2}}$, would be given by

$$q_c = \frac{\hbar^2}{16\pi M E_R^{\frac{1}{2}}} \left(1 \pm \frac{1}{2s+1} \right) \frac{\Gamma_r \Gamma_n^R}{E_R^2 + \frac{1}{4}\Gamma^2}. \quad (25)$$

This interpretation is not necessarily justified, for there may be significant contributions from more distant levels. However, one would expect q_c to vary irregularly from element to element, as it does. On the other hand, q_s includes a substantial contribution from the potential scattering. This will be proportional to the effective geometrical cross-section of the nucleus and should vary as $A^{2/3}$, where A is the mass number. q_s should therefore vary much more smoothly than q_c from element to element and tend to increase with mass number. This is in agreement with the observed results.

Summarizing the conclusions derived from the experiments we may

† Barker and Goldhaber, *Phys. Rev.* **72** (1947), 866; Seidl, Harris, and Langsdorf, *ibid.* p. 168.

‡ Harris, Langsdorf, and Seidl, *ibid.* p. 866.

take the following average values for the various constants associated with slow neutrons, i.e. with compound nuclei possessing 7-9 M.e.V. excitation energy:

Level spacing for medium to heavy nuclei	5-10 e.V.
Radiation width	0.12 e.V.
Neutron escape width (for nuclei with mass number ~ 100)	$1.4E_R^{\dagger} \times 10^{-3}$ e.V.

2.3. Resonance phenomena involving light nuclei

2.31. *Resonant collisions with medium energy neutrons.* As remarked earlier, the study of resonance phenomena in collisions of neutrons with light nuclei is as yet hardly begun. The spacing between levels is of the order of tens of kilovolts and sources of neutrons with controllable energy covering this range are only just becoming available. At the time of writing the most complete study reported is that of Seagondollar and Barschall,† who measured the total cross-section of aluminium for neutrons with energies ranging from 10 to 1,000 k.e.V. Ten resonance levels were found in this range, giving an average level spacing of 100 k.e.V. at an excitation energy of 9 M.e.V. The width of the level for 155 k.e.V. neutrons is between 16 and 35 k.e.V. This width must be due almost entirely to elastic scattering, since the radiation width is unlikely to exceed a few electron volts (see § 2.32). For comparison with neutron widths for medium and heavy nuclei, we may make use of the relation

$$\Gamma(E_1)/\Gamma(E_2) = (E_1/E_2)^{\dagger},$$

where $\Gamma(E_1)$, $\Gamma(E_2)$ refer to the neutron widths at two neutron energies E_1 , E_2 . Reduced to a neutron energy of 1 e.V., the observed width for aluminium comes out to be between 40 and 80 e.V. This is more than 10^4 times greater than for cadmium, showing once more how rapidly the width increases with decrease in the number of nuclear degrees of freedom.

2.32. *Radiative capture of protons.* The one-level formula gives for the radiative capture cross-section for this case

$$Q_c = \frac{\pi}{2k^2} \frac{\Gamma_r \Gamma_p}{(E - E_R)^2 + \frac{1}{4}\Gamma^2} \left(1 \pm \frac{1}{2s+1} \right), \quad (26)$$

where Γ_p is the partial width for re-emission of protons with their initial energy. If it is assumed that there is no appreciable possibility of the

† *Phys. Rev.* **72** (1947), 439. See also Allen, Burcham, and Wilkinson, *Proc. Roy. Soc. A*, **192** (1947), 114.

compound nucleus breaking up with emission of particles or of protons with less than the incident energy, then $\Gamma = \Gamma_r + \Gamma_p$.

The proton width Γ_p will include a factor representing the chance that the particle will penetrate the Coulomb potential barrier and may be written†

$$\Gamma_p = e^{-P} \left(\frac{E}{E_R} \right)^{\frac{1}{2}} \Gamma_p^R, \quad (27)$$

where Γ_p^R is the width, in the absence of barrier, at the resonance energy E_R . The first factor gives the chance that protons of energy E will penetrate the barrier. It is given by formula (36) of Chapter III.

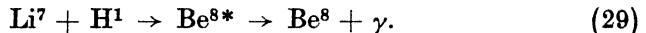
We assume, as for slow neutrons, that only protons of zero angular momentum are effective.

For light nuclei Γ_p^R is very much larger than Γ_r . Radiative capture is more important than elastic scattering only at energies so low that e^{-P} is very small. Except under these conditions we may take $\Gamma_p \simeq \Gamma$.

There is much less experimental information available on proton capture than on slow neutron absorption. Most experiments have been designed to measure primarily the resonance energies, some also give the total (effectively the proton) width and some the integrated yield over a resonance level. The latter is given by

$$\int Q_c dE = \frac{\pi^2 \Gamma_r \Gamma_p}{k^2 \Gamma} \left(1 \pm \frac{1}{2s+1} \right). \quad (28)$$

The case most thoroughly investigated is probably that of capture by Li^7 :‡



A resonance level exists at a proton energy of 440 k.e.V. and is of width 11 k.e.V. From the integrated yield Γ_r comes out to be 4 e.V., when in (28) the negative sign is taken with $s = 3/2$. For this case e^{-P} comes out to be $1/3.5$, so Γ_p^R is about 40 k.e.V. This may be reduced to the width at 1 e.V. energy by multiplying by $(4.4 \times 10^5)^{-\frac{1}{2}}$. This gives 60 e.V., to be compared with 10^{-4} e.V. for the neutron width in medium and heavy nuclei, and 40–80 e.V. in aluminium.

The resonance level of the compound nucleus Be^8 has also been studied by observing the elastic scattering of protons by lithium (see § 2.35). As Be^8 is known to be unstable against disintegration into two α -particles,§ it would appear incorrect to ignore the level width due to this possibility. Actually the expected width due to α -disintegration

† See Chap. III, § 5.1.

‡ Hafstad, Heydenburg, and Tuve, *Phys. Rev.* **49** (1936), 866; Bonner and Evans, *73* (1948), 666.

§ Dee and Gilbert, *Proc. Roy. Soc. A*, **154** (1936), 291; Wheeler, *Phys. Rev.* **59** (1941), 27.

is much higher than the observed total width, and it thus appears probable that, because of a selection rule, the α -process is forbidden in this case. This would occur if the compound level of Be^8 formed by the proton capture is of odd parity or odd total angular momentum. Further evidence in support of this viewpoint is given from the proton scattering experiments (§ 2.35 below).

Resonance energies found for proton capture by other light nuclei are given in Table III. The case of fluorine† has been investigated in

TABLE III
Resonance Levels in Nuclear Complexes formed by Proton Capture

Initial nucleus	Compound nucleus	Resonance lines		Line width (e.k.V.)	Reference
		Proton energy (e.k.V.)	Excitation energy (M.e.V.)		
Li^7	Be^8	440	17.8	11	(a), (e)
Be^8	B^{10}	350, 670	6.8, 7.1	..	(b)
B^{11}	C^{12}	180, 650, 850, 950	16.3, 16.7, 16.9, 17.0	..	(b)
C^{12}	N^{13}	480	2.5	..	(b)
C^{13}	N^{14}	570	8.2	..	(b)
F^{19}	Ne^{20}	330, 470, 590	13.3, 13.5, 13.6	..	(b), (c), (d)
		670, 860, 920	13.7, 13.9, 13.9	..	
Na^{23}	Mg^{24}	425, 525, 570	11.3, 11.4, 11.5	..	(e)
		690, 755, 875	11.6, 11.7, 11.8	..	
Mg^{25}	Al^{26}	180, 410, 480,	8.0, 8.2, 8.3	..	(e)
		575, 825	8.4, 8.6	..	
Mg^{26}	Al^{27}	580, 680, 1,000	7.7, 7.8, 8.1	..	(e)
P^{31}	S^{32}	460, 580, 700, 950	9.9, 10.0, 10.1, 10.4	..	(e)

(a) Hafstad, Hoydenburg, and Tuve, *Phys. Rev.* **49** (1936), 866.

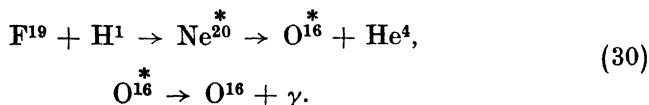
(b) Curran, Dec, and Petrzilka, *Proc. Roy. Soc. A*, **169** (1939), 269.

(c) Street, Fowler, and Lauritsen, *Phys. Rev.* **59** (1941), 253.

(d) Bennett, Bonner, Mandeville, and Watt, *ibid.* **70** (1946), 882.

(e) Curran and Strothers, *Proc. Roy. Soc. A*, **172** (1939), 72.

some detail, but the interpretation is more complicated. It has been found that the gamma radiation arises from the sequence of processes



The competing processes involved in the decay of the neon compound nucleus are emission of short-range α -particles, emission of long-range α -particles, and re-emission of protons. A theoretical discussion has been given by Schiff.‡

† Street, Fowler, and Lauritsen, *ibid.* p. 253; Bennett, Bonner, Mandeville, and Watt, *ibid.* **70** (1946), 882; Bonner and Evans, *ibid.* **73** (1948), 666.

‡ *Ibid.* **70** (1946), 891.

2.33. Resonance disintegration by α -particles. Resonance effects in nuclear collisions were first observed in disintegration of light nuclei by α -particles.† At that time they were interpreted in terms of the one-body theory according to which resonance effects would only occur if the energy of the incident α -particles was below the Coulomb barrier. With the many-body picture, this is no longer strictly valid but remains largely true in practice for the following reason. The barrier penetrability falls off very rapidly for large angular momenta. Hence the only levels of the compound nucleus which will be formed by α -particles, with energies below the barrier, will be ones with low angular momenta. These levels will be relatively widely spaced and resonance effects will not be obscured by overlap. Once the α -particles are energetic enough to pass over the barrier there is much less restriction on the angular momentum of the compound nucleus. The effective resonance levels are thus more closely spaced and tend to overlap sufficiently to obscure resonance effects.

Table IV summarizes the observations for a number of cases. The total level width is probably due largely to the emitted particle rather than to re-emission of the α -particle. In most cases more than one

TABLE IV

Resonance Levels in Nuclear Complexes formed by α -particle Capture

Initial nucleus	Compound nucleus	Resonance levels		Level width (M.e.V.)	Reference
		α -particle energy (M.e.V.)	Excitation energy of compound nucleus (M.e.V.)		
Be ⁹	C ¹³	3.4; 4.8	12.8; 13.8	0.3; 0.3	(a)
B ¹⁰	N ¹⁴	4.2	14.8	0.5	(b)
B ¹¹	N ¹⁵	3.2	13.4	0.4	(c)
N ¹⁴	F ¹⁸	3.6	8.2	0	(d)
F ¹⁹	Na ²³	3.7; 4.1	14.5; 14.8	0.10; 0.13	(e)
Mg ²⁴	Si ²⁸	5.7; 6.3	13.7; 14.2	0.12; 0.13	(e)
Al ²⁷	P ³¹	4.0; 4.5	12.0; 12.4	0.10	(f)
		4.9; 5.3	12.8; 13.1	0.07; 0.13	(g)
		5.8; 6.6	13.6; 14.3	0.12	(g)

(a) Bernadini, *Zeits. f. Physik*, **85** (1933), 555.(b) Miller, Duncanson, and May, *Proc. Camb. Phil. Soc.* **30** (1934), 549.(c) Chadwick, *Proc. Roy. Soc. A*, **142** (1933), 1.(d) Paton, *Zeits. f. Physik*, **90** (1934), 586.(e) Chadwick, Constable, and Pollard, *Proc. Roy. Soc. A*, **130** (1931), 463.(f) Chadwick and Feather, *Int. Conf. Phys.*, London (1934).(g) Duncanson and Miller, *Proc. Roy. Soc. A*, **146** (1934), 396.

† Chadwick, Constable, and Pollard, loc. cit.

group of emitted particles is observed, corresponding to different states of the final nucleus, as will be seen from the table. The mean width for a single group is obtained by dividing the total width by the number of groups. It thus appears that, for the compound nuclei C^{13} , N^{14} , and P^{31} , the proton (or neutron) width for a given final state, is about 0.1, 0.06, and 0.02 M.e.V. The average energy of the emitted particles is roughly 5 M.e.V. so the partial level widths, reduced to 1 e.V. energy, are from 25 to 50 e.V. for C^{13} and N^{14} and about 10 e.V. for P^{31} . These values are compatible with those derived from neutron collisions and from radiative capture of protons (§§ 2.31 and 2.32).

The α -particle width may be deduced also, from the integrated disintegration yield, using the formula (28) with Γ_α for Γ , provided the angular momentum of the resonance level is known. Thus it is found from the measurements for Aluminium that $\{1 + 1/(2s + 1)\}\Gamma_\alpha = 60$ k.e.V., which is to be compared with the total width of 90 k.e.V.

2.34. *Summary of data on level spacings and level widths for light nuclei.* Combining the data available from the two kinds of experiment discussed above we have, for light nuclei:

Level spacing—at about 14 M.e.V. excitation energy, ~ 1 M.e.V. for C, ~ 0.1 M.e.V. for Ne.

Particle level width (reduced to 1 e.V. energy and without barrier) ~ 60 e.V. for Be^8 , ~ 10 e.V. for P^{31} .

Radiation level width $\sim 1-5$ e.V.

2.35. *Elastic scattering of charged particles by light nuclei.* We consider first the case in which the incident and struck particles have zero spin. The formula (132) of Chapter VIII may then be applied, giving for the differential cross-section

$$|f(\theta)|^2 = \left| \frac{1}{2ik} \sum_l (2l+1) S_l P_l(\cos \theta) \right|^2, \quad (31)$$

where

$$S_l = e^{2i\eta_l} - 1 - ie^{2i\eta_l} \sum_R \frac{\Gamma_\alpha}{E - E_R + \frac{1}{2}i\Gamma}. \quad (32)$$

In this expression η_l is the phase shift due to the potential scattering which is approximately that due to an infinite potential barrier, of radius R , plus a Coulomb field. The sum is taken over the resonance levels of the compound nucleus which possess l units of angular momentum, Γ is the total width of the level E_R , and Γ_α the partial width for re-emission of the incident particle, usually an α -particle, with its initial energy.

In most instances we can ignore the effect of all but the closest

resonance level. We shall, at first, also make the further assumption that the only processes which can contribute to the total level width are elastic scattering and radiation. For light nuclei the radiation width is negligible compared with the particle width, except for very low particle energies, so we may write

$$\frac{i\Gamma_\alpha}{E - E_R + \frac{1}{2}i\Gamma} \simeq \frac{i\Gamma}{E - E_R + \frac{1}{2}i\Gamma} = 1 - e^{2i\delta_l}, \quad (33)$$

where
$$\delta_l = \arctan\left(\frac{\frac{1}{2}\Gamma}{E_R - E}\right). \quad (34)$$

This gives
$$S_l = e^{2i\psi_l} - 1, \quad (35)$$

with
$$\psi_l = \eta_l + \delta_l. \quad (36)$$

The expression for the differential cross-section thus takes the standard form (cf. (17) of Chap. II) with the phase shift given by the sum of a contribution from the potential scattering and from the neighbouring resonance level.

For scattering of charged particles the quantity of most interest is the ratio R of the differential cross-section to that which would be given by the Coulomb field only. Following a similar procedure to that used in discussing proton-proton collisions, we find

$$R = \left| 1 + \frac{i}{\alpha} \sin^2 \frac{1}{2}\theta \exp(i\alpha \log \sin^2 \frac{1}{2}\theta) \sum e^{2i(\zeta_l - \zeta_0)} (e^{2i\kappa_l} - 1)(2l+1)P_l(\cos \theta) \right|^2, \quad (37)$$

where $\alpha = ZZ'\epsilon^2/\hbar v$, Z, Z' being the nuclear charges and v the relative velocity. ζ_l is the phase shift due to the pure Coulomb field, given by (see Chap. III, § 4.1)

$$\zeta_l = \arg \Gamma(l+1+i\alpha). \quad (38)$$

Thus
$$e^{2i(\zeta_l - \zeta_0)} = \frac{(1+i\alpha)^2(2+i\alpha)^2 \dots (l+i\alpha)^2}{(1+\alpha^2)(2^2+\alpha^2) \dots (l^2+\alpha^2)}. \quad (39)$$

κ_l is the additional phase shift due to the resonance scattering and the remainder of the potential scattering so that

$$\kappa_l = \eta_l + \delta_l - \zeta_l. \quad (40)$$

In general $\eta_l - \zeta_l$ will vary smoothly and gradually with energy. It follows from the form (34) of δ_l that, in passing through a resonance level, κ_l will change by $\frac{1}{2}\pi$. If it is possible to carry out measurements of the ratio R over such an energy and angular range that the phases κ_l may be deduced, the energy and width of resonance levels may be obtained from this result.

The only collisions for which a sufficiently complete series of observations have been carried out for an analysis of this kind are those of α -particles with helium nuclei.† Allowance must be made in this case for the symmetry of the system which requires that the contribution from odd angular momenta should vanish (see Chap. V, § 4.1). The theoretical analysis due to Wheeler‡ leads to the phase shifts illustrated in Fig. 62. The behaviour of κ_0 strongly indicates the existence of a

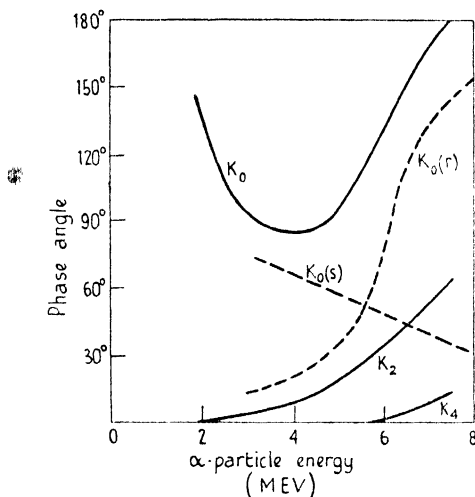


FIG. 62. Phase angles derived from analysis of anomalous scattering of α -particles by helium. $\kappa_0(r)$ and $\kappa_0(s)$ are the two components of κ_0 arising respectively from a resonance level of Be^8 and from potential scattering.

resonance level. Evidence from the α -disintegration of Be^8 already indicated the existence of a level at 2.8 M.e.V. with width 0.8 M.e.V. Wheeler showed that the derived κ_0 could be well represented by taking δ_0 as given by (34) with $E_R = 3.1$ M.e.V. and $\Gamma = 0.8$ M.e.V., leaving a contribution from $\eta_0 - \zeta_0$ which varied linearly with energy over the resonance region. This is roughly what would be expected on the basis of the rigid sphere representation of the anomalous potential scattering. The decomposition of κ_0 into these two contributions is illustrated in Fig. 62.

The collisions of α -particles with O^{16} and C^{12} nuclei also satisfy the conditions for applicability of the formula (31). Up to the present the

† Rutherford and Chadwick, *Phil. Mag.* **4** (1927), 605; Chadwick, *Proc. Roy. Soc. A*, **128** (1930), 120; Blackett and Champion, *ibid. A*, **130** (1931), 380; Wright, *ibid. A*, **137** (1932), 677; Mohr and Pringle, *ibid.* **160** (1937), 193; Devons, *ibid. A*, **172** (1939), 564.

‡ *Phys. Rev.* **59** (1940), 16.

study of these collisions has been confined to observation† of the energy variation of the scattering ratio at a limited number of fixed angles. Resonance effects appear in such observations as maxima in the scattering as the energy varies. In the neighbourhood of a resonance level with l units of angular momentum the scattering ratio R may be written

$$R = \left| ae^{i\xi} + \frac{\rho e^{i\sigma}}{x+i} \right|^2, \quad (41)$$

where

$$\begin{aligned} \rho &= 2(2l+1)\alpha^{-1} \sin^2 \frac{1}{2}\theta P_l(\cos \theta), \\ \sigma &= \alpha \log 2 \sin^2 \frac{1}{2}\theta + \zeta_l - \zeta_0, \quad x = 2(E - E_R)/\Gamma. \end{aligned} \quad (42)$$

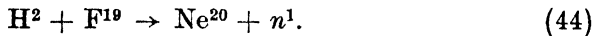
$ae^{i\xi}$ represents the contribution from the background scattering. If we ignore the relatively slow variation of this background scattering with energy, we find that the maximum and minimum values of R in the neighbourhood of the resonance level are given by

$$\begin{aligned} R_{\max}^{\dagger} &= \{a^2 - a\rho \sin(\sigma - \xi) + \frac{1}{4}\rho^2\}^{\dagger} + \frac{1}{2}\rho, \\ R_{\min}^{\dagger} &= \{a^2 - a\rho \sin(\sigma - \xi) + \frac{1}{4}\rho^2\}^{\dagger} \sim \frac{1}{2}\rho, \end{aligned}$$

so that

$$\rho = R_{\max}^{\dagger} \pm R_{\min}^{\dagger}. \quad (43)$$

The variation of R in passing through the level is as shown in Fig. 63. If the observations are made at large angles, so that ρ is large, the maximum occurs very nearly at the resonance energy, the minimum at an energy less than the resonance value by $\frac{1}{2}\Gamma\rho \sec(\sigma - \xi)a$. From observations of this kind it is possible to observe resonance energies, but it is more difficult to decide the angular momentum of the level concerned—it is usually difficult to determine ρ from (43) as the cross-section minimum is often obscured by insufficient resolution. Fig. 64 illustrates results obtained by Ferguson and Walker‡ for scattering at 157° by oxygen. Two distinct resonances at 6.5 and 5.5 M.e.V. are clearly seen. These levels arise from excited states of Ne^{20} at 10.1 and 9.0 M.e.V. above the ground state and have also been observed by Bonner§ in the reaction



Similar measurements for carbon reveal levels which correspond to excited states of O^{16} at 11.4, 11.1, and 10.6 M.e.V. above the ground state. Much still remains to be done in studying these scattering phenomena over a wide range both of energy and of angle.

For collisions in which the nuclei do not possess zero spin the general

† See, for example, Devons, *Proc. Roy. Soc. A*, **172** (1939), 127, and Ferguson and Walker, *Phys. Rev.* **58** (1940), 666.

‡ *Ibid.*

§ *Proc. Roy. Soc. A*, **174** (1940), 339.

formula is more complicated, but much may still be done in analysing the resonance effects by ignoring the potential scattering, provided the ratio R at resonance maximum is considerably greater than unity.

The most interesting experiments of this kind involve the scattering of neutrons or of protons. Staub and Stephens† observed a resonance maximum in the scattering of 1 M.e.V. neutrons by helium nuclei. It was later found by Staub and Tatel‡ that the resonance level was a

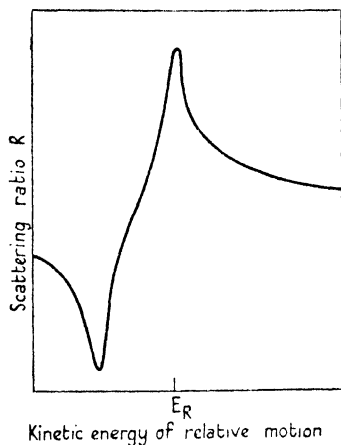
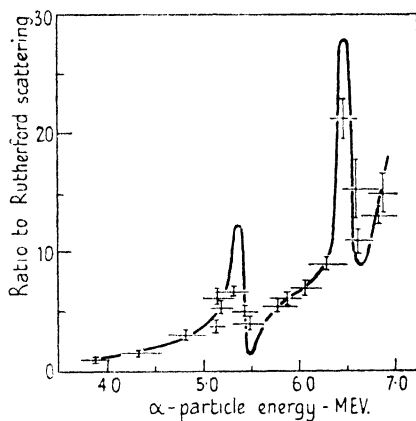


FIG. 63.

FIG. 64. Anomalous scattering of α -particles by oxygen at 157° , exhibiting two resonance levels of Ne^{20} .

doublet of width 0.4 M.e.V. The magnitude of the cross-section indicates that neutrons with one unit of angular momentum are involved. This being so, the resonance levels are those of the $P^{\frac{1}{2}}$, $P^{\frac{3}{2}}$ doublet of He^5 . Further evidence for this result has been deduced by Wheeler and Barschall§ from the experimental results of Barschall and Kanner.|| The corresponding resonance has been observed in proton scattering by helium,†† and, although too broad to resolve into doublets, can be identified as a P level of Li^5 .

So far it has been assumed that the partial width Γ_p for elastic scattering is practically equal to the total width Γ of the resonance level. If this is not so, a factor Γ_p/Γ must be included in the expression (43) for ρ , thereby reducing the importance of the resonance effect. This will be so in scattering by heavy nuclei where inelastic collisions are important. It

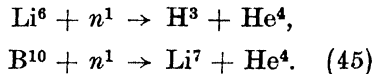
† *Phys. Rev.* **55** (1939), 131.‡ *Ibid.* **58** (1940), 820.§ *Ibid.* p. 682.|| *Ibid.* p. 590. See, however, Hall and Koontz, *ibid.* **72** (1947), 196.†† Heydenburg and Ramsey, *ibid.* **60** (1941), 42.

also means that in the elastic scattering of deuterons, which, owing to their high internal energy, usually produce disintegration on collision, resonance effects will be very weak.

An application of these considerations has been made by Creutz,† who investigated the scattering of protons by lithium. He observed the resonance level which is effective in the radiative capture process (see (29) above). The magnitude of the effect indicated that Γ_p/Γ is of order unity. This makes it unlikely that the state of the compound Be^8 nucleus which is formed can break up by α -particle emission, in agreement with the conclusions of § 2.32.

2.36. Particle emission from light nuclei after capture of slow neutrons.

There are two reactions in which slow neutron capture leads to α -particle emission:



The boron reaction is of special importance in practice. This is because the cross-section is large and follows the inverse velocity law up to quite high neutron energies. It therefore provides a convenient method for measuring neutron flux over a wide

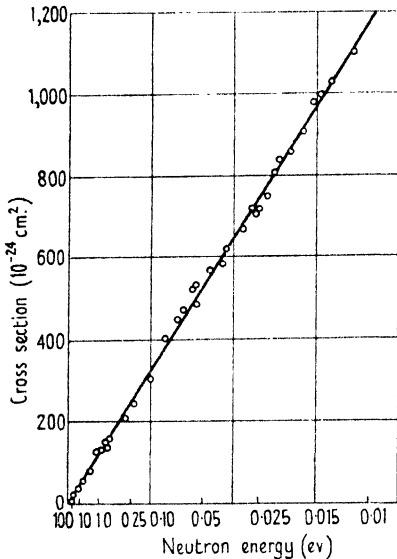


Fig. 65. Observed total cross-section for absorption of slow neutrons in boron showing that it is inversely proportional to the neutron velocity.

range of conditions. Fig. 65 illustrates the observed variation of the boron cross-section over a neutron energy range from 0.01 to 100 e.v. obtained by Rainwater and Havens‡ using the modulated beam method.

The α -particles emitted in the two reactions are quite energetic and are able to pass over the Coulomb potential barrier. It is reasonable to suppose therefore that the appropriate partial width Γ_α is of the same order as it would be for neutrons of the same energy. In applying the one-level formula

$$Q_c = \frac{\pi}{2k^2} \left(1 \pm \frac{1}{2s+1} \right) \frac{\Gamma_\alpha \Gamma_n}{(E - E_R)^2 + \frac{1}{4}(\Gamma_\alpha + \Gamma_n + \Gamma_r)^2}, \quad (46)$$

† *Phys. Rev.* **55** (1939), 819.

‡ *Ibid.* **70** (1946), 136; see also Zinn, *ibid.* **71** (1947), 752.

we may write

$$\Gamma_n = a\Gamma_\alpha(E/E_\alpha)^{\frac{1}{2}},$$

where a is of order unity. The radiation width Γ_r may be ignored as it is very small compared with Γ_α . This gives

$$Q_c = \frac{\hbar^2}{16\pi M} \frac{a}{(EE_\alpha)^{\frac{1}{2}}} \frac{\Gamma_\alpha^2}{E_R^2 + \frac{1}{4}\Gamma_\alpha^2} \left(1 \pm \frac{1}{2s+1}\right), \quad (47)$$

where M is the neutron mass. The observed value for boron is† $6.41 \times 10^{-22} E^{-\frac{1}{2}} \text{ cm.}^2$, where E is measured in e.V., so that $a\Gamma_\alpha^2/(E_R^2 + \frac{1}{4}\Gamma_\alpha^2)$ comes out to be 8.5. This shows that Γ_α is probably of the same order as E_R . It is known that Γ_α is of the order 100,000 e.V. (see § 2.33), so that E_R is probably of this order also. The smaller cross-section observed for the lithium reaction‡ is probably due to the effective resonance energy being larger.

3. Effect of molecular binding on the scattering of slow neutrons

3.1. The pseudo-potential

So far we have considered the collisions of neutrons with free nuclei. The conclusions will remain valid if the nuclei are bound in chemical compounds, provided the binding energy is small compared with the kinetic energy of the neutrons. If this condition is not satisfied modifications due to the binding become important. In this section we discuss the way in which these effects may be taken into account.

The problem of the exchange of energy between translational motion of an atom and molecular vibration was discussed in Chap. XII, § 3.5. It was stated there that, provided the range of the interaction between the impinging atom and the particular atom in the molecule with which the impact occurs is great compared with the amplitude of the vibration, Born's first approximation may be used. For the neutron problem, however, the state of affairs is the very opposite to this—the range of interaction is very small compared to the amplitude of vibration. Nevertheless, Fermi§ showed that Born's approximation may still be used if the actual interaction between a neutron of mass m and nucleus of mass M is replaced by a pseudo-potential

$$V_{ps} = -\frac{\hbar^2}{\pi} \frac{M+m}{Mm} a \delta(\mathbf{r}), \quad (48)$$

where \mathbf{r} is the relative position vector of the neutron and nucleus, $4\pi a^2$

† Ibid.

‡ Havens and Rainwater, *Phys. Rev.* **70** (1946), 154.

§ *Ric. Sci.* **7** (1936), 13.

is the low velocity limit of the scattering cross-section when the nucleus is free, and δ is the usual δ -function.

Before showing how this may be justified it is of interest to state certain general consequences. If Q_0 is the neutron scattering cross-section for the free nucleus at rest, or for the bound nucleus when the neutron energy is great compared with that of the molecular vibration and rotation, the cross-section for scattering of neutrons with energy insufficient to excite even molecular rotation is greater than Q_0 by a factor $(1+m/M)^2/(1+m/M_1)^2$, where M_1 is the mass of the molecule as a whole. Thus the cross-section for scattering of a very slow neutron by a proton bound to an infinite mass is four times greater than that for a free proton at rest.

For intermediate conditions the effect is more complicated. When the neutron energy is sufficient to excite vibration, a quantum treatment using Born's approximation is necessary. In most practical cases the neutron energy is great compared with that of the rotation and, if no vibrational excitation can occur, it is possible to deal with the problem classically. The reduced mass $(mM_1)/(m+M_1)$ which occurs in the factor above is then replaced by a mass tensor so that the effect depends on the direction of incidence of the neutron relative to the molecules. Special interest attaches to collisions with molecular hydrogen and, to a lesser extent, with deuterium, as the rotational energy is then comparable with the kinetic energy of neutrons at liquid air temperature.

In a complete treatment of the scattering of neutrons by molecules and by crystals it is necessary to allow also for interference effects, for the dependence of the cross-section on nuclear spin, and, in certain cases, for capture. The first two of these are of particular importance for molecular hydrogen and deuterium.

We shall first show how the use of Fermi's pseudo-potential may be justified and then describe briefly some applications.

3.11. Derivation of the pseudo-potential.† For the sake of definiteness we take the case of a neutron colliding with a proton which is under the influence of a molecular binding potential. The wave equation for the system may be written

$$\left[\frac{\hbar^2}{8\pi^2 M} (\nabla_p^2 + \nabla_n^2) + E - V(\mathbf{r}_p) - U(|\mathbf{r}_p - \mathbf{r}_n|) \right] \Psi = 0, \quad (49)$$

where M is the mass of either nucleon, \mathbf{r}_p , \mathbf{r}_n are the respective coordinates of neutron and proton, U is the nuclear interaction between them, and $V(\mathbf{r}_p)$ is the potential energy of the proton due to the molecular binding. The range of U is

† The method of this section follows closely that given in greater detail by Breit, *Phys. Rev.* **71** (1947), 215.

not only much smaller than the wave-length of the incident neutron but is also much smaller than the amplitude of the proton oscillations.

We require solutions of the equation (49) of the usual form

$$\Psi = \sum F_s(\mathbf{r}_n)\psi_s(\mathbf{r}_p), \quad (50)$$

$$\text{where } F_s \sim r_n^{-1}e^{ik_s r_n} f_s(\theta_n, \phi_n), \quad F_0 \sim e^{ik_z n} + r_n^{-1}e^{ik_r n} f_0(\theta_n, \phi_n). \quad (51)$$

$\psi_s(\mathbf{r}_p)$ is the vibrational wave function of the proton in the field V , associated with energy E_s , so that

$$k_s^2 = 2M(E - E_s)/\hbar^2$$

It follows from equation (16) of Chapter VIII and (30) of Chapter VI that

$$F_s = -\frac{2\pi M}{\hbar^2} \iint U(r') \frac{\exp\{ik_s|\mathbf{r}_n - \mathbf{r}'_n|\}}{|\mathbf{r}_n - \mathbf{r}'_n|} \Psi(\mathbf{r}'_p, \mathbf{r}'_n) \psi_s^*(\mathbf{r}'_p) d\tau'_p d\tau'_n, \quad (52)$$

where we denote $\mathbf{r}_p - \mathbf{r}_n$ by \mathbf{r} . Substituting back in (50) gives, without approximation

$$\Psi = e^{ik_z n} \psi_0 - \frac{2\pi M}{\hbar^2} \sum_s \psi_s \iint U(r') \frac{\exp\{ik_s|\mathbf{r}_n - \mathbf{r}'_n|\}}{|\mathbf{r}_n - \mathbf{r}'_n|} \Psi(\mathbf{r}'_p, \mathbf{r}'_n) \psi_s^*(\mathbf{r}'_p) d\tau'_p d\tau'_n. \quad (53)$$

We now take advantage of the possibility of choosing a range R such that, while $U(r')$ is relatively very small for $r' \simeq R$ it is large compared with the energy of molecular vibration for $r' < R$.

By changing the variables from $\mathbf{r}_p, \mathbf{r}_n$ to \mathbf{r}_p, \mathbf{r} we may expand Ψ in the alternative form

$$\Psi = \sum \psi_s(\mathbf{r}_p) \chi_s(\mathbf{r}),$$

$$\text{where } \left[\frac{\hbar^2}{4\pi^2 M} \nabla^2 - U + E - E_s \right] \chi_s = -\frac{\hbar^2}{2\pi M} \sum_t \nabla_{st} \cdot \nabla \chi_t,$$

$$\text{with } \nabla_{st} = \int \psi_s^* \nabla_p \psi_t d\tau_p. \quad (54)$$

Within the range R of U , $E - E_s$ is negligible. So also is the sum on the right-hand side, for the change of the proton functions ψ_s, ψ_t is negligible between 0 and R . We may therefore take χ_s as a proper solution χ of

$$\left[\frac{\hbar^2}{4\pi^2 M} \nabla^2 - U \right] \chi = 0, \quad (55)$$

for all s , so that, within the range R of U , Ψ may be written

$$\Psi = f(\mathbf{r}_p) \chi(\mathbf{r}). \quad (56)$$

Substitution in (53) gives now

$$\Psi = e^{ik_z n} \psi_0 - \frac{2\pi M}{\hbar^2} \sum_s \psi_s \int f(\mathbf{r}'_p) G(\mathbf{r}, \mathbf{r}'_p, \mathbf{r}_p) \psi_s^*(\mathbf{r}'_p) d\tau'_p, \quad (57)$$

$$\text{with } G(\mathbf{r}, \mathbf{r}'_p, \mathbf{r}_p) = \int \frac{\exp\{ik_s|\mathbf{r}_n - \mathbf{r}'_n|\}}{|\mathbf{r}_n - \mathbf{r}'_n|} U(r') \chi(\mathbf{r}') d\tau'. \quad (58)$$

Within the range R of U , $|\mathbf{r}'_n - \mathbf{r}'_p| < R$, so that

$$G(\mathbf{r}, \mathbf{r}'_p, \mathbf{r}_p) \simeq \frac{\exp\{ik_s|\mathbf{r}_n - \mathbf{r}'_p|\}}{|\mathbf{r}_n - \mathbf{r}'_p|} I, \quad (59)$$

where

$$I = \int U(r') \chi(\mathbf{r}') d\tau'. \quad (60)$$

This integral may be evaluated using the equation (55) for χ , to give

$$I = -\frac{\hbar^2 a}{\pi M}, \quad (61)$$

where a is the value of $-r^2 d\chi/dr$ at $r = R$, beyond which U vanishes.

We now have

$$\Psi = e^{ikz_n} \psi_0 + 2a \sum \psi_s(\mathbf{r}_p) \int \psi_s^*(\mathbf{r}'_p) f(\mathbf{r}'_p) \frac{\exp\{ik_s |\mathbf{r}'_p - \mathbf{r}_n|\}}{|\mathbf{r}'_p - \mathbf{r}_n|} d\tau'_p, \quad (62)$$

so that, to this approximation,

$$\left[\frac{\hbar^2}{8\pi^2 M} (\nabla_p^2 + \nabla_n^2) + E - V(\mathbf{r}_p) \right] \Psi = -\frac{a\hbar^2}{\pi M} f(\mathbf{r}_p) \delta(\mathbf{r}_p - \mathbf{r}_n). \quad (63)$$

It is now only necessary to obtain a suitable approximation for $f(\mathbf{r}_p)$. To do this we note that, ignoring a^2 , and except for very small r ,

$$\chi \simeq \left(1 + \frac{a}{r}\right) \quad (r < R). \quad (64)$$

Substituting

$$\Psi = \chi(r) f(\mathbf{r}_p) = \left(1 + \frac{a}{r}\right) f(\mathbf{r}_p), \quad (65)$$

on the left-hand side of (62) and writing

$$\frac{f(\mathbf{r}_p)}{|\mathbf{r}_p - \mathbf{r}_n|} = \sum \psi_s(\mathbf{r}_p) \int \frac{f(\mathbf{r}'_p) \psi_s^*(\mathbf{r}'_p) d\tau'_p}{|\mathbf{r}'_p - \mathbf{r}_n|}, \quad (66)$$

gives

$$f(\mathbf{r}_p) = e^{ikz_n} \psi_0(r_p) + O(a). \quad (67)$$

The equation (63) with the form (67) for $f(\mathbf{r}_p)$ is of exactly the same form as that which would have been obtained if the neutron-proton interaction were represented by the potential

$$V_{ps} = -\frac{a\hbar^2}{\pi M} \delta(\mathbf{r}_p - \mathbf{r}_n), \quad (68)$$

and Born's approximation applied, so that $V_{ps} \Psi$ is replaced by $V_{ps} \psi_0(r_p) e^{ikz_n}$.

In this way a solution is obtained which is essentially the first term of an expansion in powers of a/d , where d is the amplitude of molecular vibrations.

3.12. Inclusion of spin coupling in the pseudo-potential. In many cases the amplitude a which appears in the pseudo-potential depends on the total spin of the neutron and scattering nucleus. It is then necessary to allow for two amplitudes $a_{s+\frac{1}{2}}$, $a_{s-\frac{1}{2}}$ according as the total spin is $s \pm \frac{1}{2}$, s being the nuclear spin quantum number. The pseudo-potential may then be written

$$-\frac{\hbar^2}{\pi M} \left[\frac{1}{2} a_{s+\frac{1}{2}} (1 + \rho) + \frac{1}{2} a_{s-\frac{1}{2}} (1 - \rho) \right] \delta(\mathbf{r}_p - \mathbf{r}_n), \quad (69)$$

where ρ is an operator possessing the respective eigenvalues ± 1 when the system has spin $s \pm \frac{1}{2}$. If σ is the spin operator for the neutron and \mathbf{s} for the nucleus, then

$$\rho = \frac{1}{2s+1} \left[1 + \frac{2\sigma \cdot \mathbf{s}}{2s+1} \right]. \quad (70)$$

3.2. Applications of the pseudo-potential

3.21. *Collisions with an isotropic vibrator.* To obtain a general idea of the way in which the total collision cross-section and rate of energy loss varies with neutron energy in passing from the limit for very slow neutrons to that in which the proton may be regarded as free, it is convenient to take the simplest case of a proton, bound isotropically to an infinitely massive atom.

The differential cross-section $I_{0s}(\theta)$ for a collision in which the proton is excited from the ground to the s th vibrational state, is given by the formula (31) of Chapter VIII, with the pseudo-potential (48) in place of $V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)$. Hence

$$\begin{aligned} I_{0s}(\theta) &= \frac{k_s}{k} \left| 2a \int \psi_0(r_p) \delta(\mathbf{r}_p - \mathbf{r}_n) \exp\{i(k\mathbf{n}_0 - k_s \mathbf{n}_s) \cdot \mathbf{r}_n\} \psi_s^*(\mathbf{r}_p) d\tau_p d\tau_n \right|^2 \\ &= (2a)^2 \frac{k_s}{k} \left| \int \psi_0(r_p) e^{iK\mathbf{n} \cdot \mathbf{r}_p} \psi_s^*(\mathbf{r}_p) d\tau_p \right|^2, \end{aligned} \quad (71)$$

where k, k_s are the initial and final wave numbers of the neutron, ψ_0, ψ_s the initial and final vibrational wave functions of the proton,

$$k\mathbf{n}_0 - k_s \mathbf{n}_s = K\mathbf{n},$$

and

$$K^2 = k^2 + k_s^2 - 2kk_s \cos \theta. \quad (72)$$

In the limit of very low neutron energies, only elastic collisions are possible and $K \rightarrow 0$, giving for the cross-section

$$\int I_{00}(\theta) d\omega = 16\pi a^2 = 4Q_0, \quad (73)$$

where Q_0 is the cross-section for collision with a free proton at rest.

For an isotropic oscillator of mass m with fundamental frequency ν , we have

$$\psi_n = \phi_{s_1}(x) \phi_{s_2}(y) \phi_{s_3}(z), \quad (74)$$

where $s_1 + s_2 + s_3 = s$ and the ϕ 's are the usual harmonic oscillator wave functions

$$\phi_s(x) = (\alpha^2/\pi)^{\frac{1}{2}} (s!)^{-\frac{1}{2}} 2^{-\frac{1}{2}s} e^{-\frac{1}{2}\xi^2} \frac{d^s}{d\xi^s} (e^{-\xi^2}), \quad (75)$$

with $\xi = (2\pi m/\hbar)^{\frac{1}{2}} x = \alpha x$.

Substitution in (71) gives

$$I_{0s}(\theta) d\omega = 4a^2 \frac{k_s}{k} e^{-q^2} \sum \frac{q_x^{s_1} q_y^{s_2} q_z^{s_3}}{s_1! s_2! s_3!} d\omega, \quad (76)$$

where $q = K\{\hbar/(4\pi m\nu)\}^{\frac{1}{2}}$ and the summation extends over all positive integral values of s_1, s_2, s_3 , for which $s_1 + s_2 + s_3 = s$. The sum may be easily carried out to give

$$I_{0s}(\theta) d\omega = 4a^2 \frac{k_s}{k} \frac{q^{2s} e^{-q^2}}{s!} d\omega. \quad (77)$$

The cross-section for the collision is now given by

$$\begin{aligned}
 Q_{0s} &= 2\pi \int_0^\pi I_{0s}(\theta) \sin \theta \, d\theta \\
 &= \frac{4\pi^2 m v}{\hbar k k_s} \int_{q_{\min}}^{q_{\max}} I_{0s} \, dq^2 \\
 &= \frac{4\pi a^2}{\epsilon} [f(q_{\min}^2) - f(q_{\max}^2)], \tag{78}
 \end{aligned}$$

where
$$f(x) = e^{-x} \left[1 + \frac{x}{1!} + \frac{x^2}{2!} + \dots + \frac{x^s}{s!} \right], \tag{79}$$

and $\epsilon = E/\hbar v$, E being the energy of the incident neutron. q_{\min} and q_{\max} may be conveniently expressed in the form

$$q_{\min} = \epsilon^\dagger - (\epsilon - s)^\dagger, \quad q_{\max} = \epsilon^\dagger + (\epsilon - s)^\dagger. \tag{80}$$

For large E , q_{\min} is $O(1/E)$ and q_{\max} is $O(E^\dagger)$, so that $f(q_{\max})$ is negligible and $f(q_{\min}) \simeq 1$ for all values of s such that $s\hbar v < E$. The cross-section is thus independent of s and approximately given by Q_0/s_0 , where $s_0\hbar v \simeq E$. Since there are approximately s_0 levels which can be excited, the total cross-section becomes Q_0 . This is just what would be expected for collisions with a free proton—all energy losses up to the total energy are equally probable and the total cross-section is Q_0 .

Fig. 66 illustrates the variation with energy of the cross-sections for intermediate values of ϵ ranging from 0 to 3. In this figure the effect of the binding on the energy loss is illustrated by a curve giving the ratio of the energy loss to that which would have occurred, on the average, in collision with a free proton.

More detailed calculations allowing for lack of symmetry in the binding, etc., have been carried out by Arley,[†] Bethe,[‡] and Sachs and Teller.[§] The latter authors considered the important practical case, mentioned earlier, in which the neutron energy, while insufficient to excite vibration, is nevertheless great compared with that of the rotational quanta.

Detailed comparison of theoretical predictions with experiment cannot yet be made except for collisions with molecular hydrogen (see § 3.22). Qualitative evidence in favour of the general conclusions is available, however, from experiments such as those of Carroll.^{||} He measured the cross-section per proton for neutrons of approximately

[†] *Kgl. Dansk. Vid. Selsk.* **16** (1938), 1.

[‡] *Rev. Mod. Phys.* **9** (1937), 126.

[§] *Phys. Rev.* **60** (1941), 18.

^{||} *Ibid.* p. 702.

thermal velocities, scattered by a series of gaseous paraffins at room temperature, and found a slow but steady increase in going from methane (CH_4) to butane C_4H_{10} . If only elastic collisions were possible, the cross-section should increase as the square of the reduced mass. It actually increases rather more slowly, but it must be remembered that excitation of rotation may still occur and the effective reduced mass must include a contribution from rotational inertia.

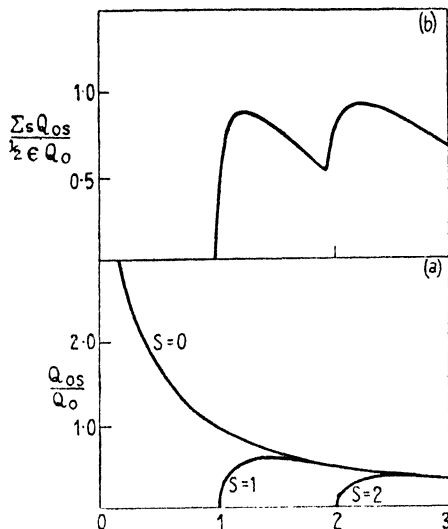


FIG. 66. Effect of chemical binding on scattering and energy loss of neutrons in collisions with protons.

- (a) Cross-sections Q_{0s} for collisions in which s vibrational quanta $h\nu$ are excited, as functions of the ratio ϵ of neutron energy to $h\nu$. Q_{0s} is given as a multiple of the cross-section Q_0 for scattering by free protons.
- (b) Effective cross-sections $\sum_s s h\nu Q_{0s}$ for energy loss in terms of that $\frac{1}{2} \epsilon h\nu Q_0$ for scattering by free protons at rest.

3.22. Collisions of slow neutrons with molecular hydrogen and deuterium.

Particular interest attaches to the study of these collisions. The simplicity of the molecules makes possible a detailed treatment of the effect of interference, as well as of the molecular binding, on the scattering. Furthermore, the rotational quanta are comparable with the energy of neutrons at room temperature, the neutron-proton interaction is spin dependent, and it is possible to study separately the scattering by molecules in which the nuclear spins are parallel or antiparallel respectively.

From a comparison of theoretical and observed cross-sections it has

proved possible to determine whether the 1S state of the deuteron (§ 1.1) is real or virtual, and it seems likely that a sensitive method of determining the range of nuclear forces may also be provided.

The rotational energy states (quantum number J) of the ground vibrational level of H_2 are divided into two non-combining sets of opposite symmetry. In para-hydrogen the nuclear spins are opposite and the rotational states symmetrical ($J = 0, 2, \dots$), whereas in ortho-hydrogen the spins are parallel and the rotational states antisymmetrical ($J = 1, 3, \dots$). The energy separation of the lowest states of the two systems is 0.0147 e.V. The rate at which ortho-hydrogen molecules can make transitions to form para molecules is so slow that it is possible, with suitable experimental technique, to carry out experiments at low temperatures in a quasi-equilibrium in which both sets are in their lowest states. It is also possible to vary the relative concentration of the two and thus to determine the separate contributions from each.

Because of the spin dependence of the interaction between a neutron and proton, a neutron impact can produce a transition between ortho and para states. If the molecules are in their lowest states and the neutron energy is < 0.0220 e.V., it is insufficient to excite a para molecule to the lowest ortho state. The only possible collisions which can then occur are either elastic, or superelastic in which an ortho molecule undergoes a transition to the para state, giving the excess energy to the neutron.

To evaluate these cross-sections the interaction between a neutron and proton may be represented by the appropriate pseudo-potential and Born's approximation used. For this case, in which $s = \frac{1}{2}$, the interaction between a neutron and a molecular proton, each of mass m , can be written

$$V = \frac{\hbar^2}{4\pi m} \{a_1(3 + \sigma_n \cdot \sigma_p) + a_0(1 - \sigma_n \cdot \sigma_p)\} \delta(\mathbf{r}_n - \mathbf{r}_p), \quad (81)$$

σ_n, σ_p being the respective spin operators of proton and neutron. The interaction with the molecule will then be given by the sum of two such terms for the two protons. It can be broken up into two parts, respectively symmetric and antisymmetric in the proton spins. The former gives rise to collisions in which the rotational symmetry is unchanged, whereas the latter leads to transitions from one system to the other.

The detailed calculation then follows along standard lines using Born's approximation with the appropriate rotational wave functions. It was first carried out in detail by Schwinger and Teller† and later carried out

† *Phys. Rev.* **52** (1937), 286.

to greater accuracy by Hamermesh and Schwinger.† It is easily seen that the three cross-sections $Q(0 \rightarrow 0)$, $Q(1 \rightarrow 1)$, and $Q(1 \rightarrow 0)$ corresponding, respectively, to elastic collisions with para and ortho molecules in their lowest states and to superelastic collisions with an ortho molecule, depend in quite different ways on the amplitudes a_1 and a_0 . They contain the factors $(3a_1 + a_0)^2$, $(3a_1 + a_0)^2 + 2(a_1 - a_0)^2$, and $(a_1 - a_0)^2$ respectively. It has been pointed out in § 1.1 that a_0 is considerably

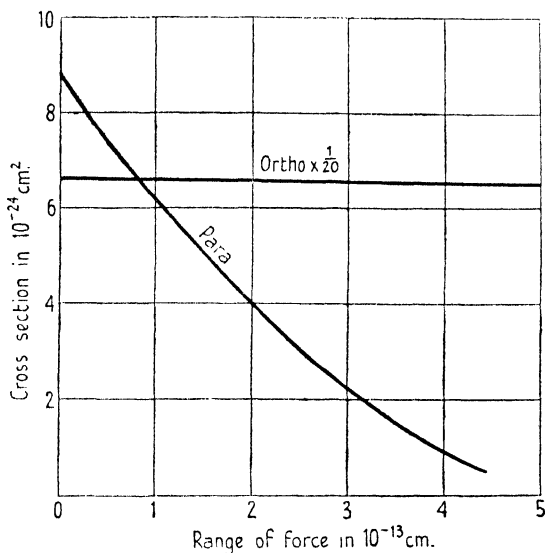


FIG. 67. Dependence of cross-section for scattering of neutrons by para- and ortho-hydrogen on the range of the neutron-proton interaction, assumed to be of spherical well form. The gas is taken to be at a temperature $T = 20^\circ$ and the neutron energy $= kT$.

greater than a_1 , so that $3a_1$ and a_0 are comparable. The para-hydrogen cross-section should thus depend very strongly on the relative sign of a_1 and a_0 , being small if the signs are opposite, i.e. if the 1S state of the deuteron is virtual. Furthermore, if the signs are opposite, as in fact they are, the size of the factor $3a_1 + a_0$ will depend quite sensitively on the magnitude of a_1 , i.e. on the range of the nuclear forces. On the other hand, the ortho-hydrogen cross-section should not depend very sensitively on the range and be relatively unaffected by cancellation. Fig. 67 illustrates these results.

The first measurements of the relative cross-sections of para- and ortho-hydrogen were carried out using liquid hydrogen, and showed clearly that the para cross-section is much smaller than the

† Ibid. 71 (1947), 679.

ortho.† This confirmed the virtual character of the 1S level of the deuteron. At the time of writing, experiments of sufficient accuracy to provide information on the range of the interaction in the 3S state are still awaited.‡

Similar calculations may be carried out for D_2 ,§ but less interesting information is likely to be derived from them. Fig. 68 illustrates the ratio of the ortho to the para cross-sections in this case, for neutrons

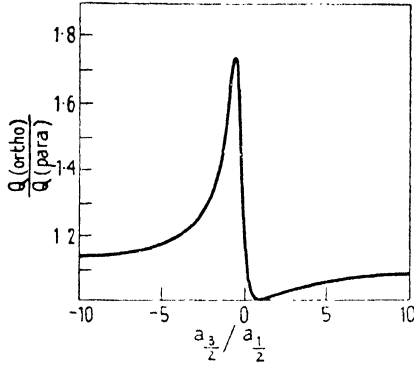


FIG. 68. Ratio $Q(\text{ortho})/Q(\text{para})$ of cross-sections for scattering of neutrons by ortho- and para-deuterium as a function of the ratio $a_{\frac{3}{2}}/a_{\frac{1}{2}}$ of the amplitudes of the quartet and doublet scattering of a neutron by a deuteron. The gas temperature and neutron energy is as in Fig. 67.

at a temperature of 20° K, as a function of the ratio $a_{\frac{3}{2}}/a_{\frac{1}{2}}$ of the amplitudes for the quartet and doublet scattering of a neutron by a deuteron. Even with experiments of the necessary accuracy the amplitude ratio cannot be determined unambiguously in this way, though the relative sign can be.

3.23. Interference effects—the sign of the scattered amplitude. It has been clear from the case of molecular hydrogen that interference effects arising from the coherent scattering of neutrons by nuclei are affected strongly by spin dependence of the forces and by the sign of the scattered amplitudes a .

Referring to the pseudo-potential (69) it may easily be seen that, whereas the total scattering depends on

$$\{(s+1)a_{s+\frac{1}{2}}^2 + sa_{s-\frac{1}{2}}^2\}(2s+1)^{-1}, \quad (82)$$

† Halpern, Estermann, Simpson, and Stern, *Phys. Rev.* **52** (1937), 142; Brickwedde, Dunning, Hoge, and Manley, *ibid.* **54** (1938), 266; Libby and Long, *ibid.* **55** (1938), 339.

‡ See, however, Sutton, Hall, Anderson, Bridge, de Wire, Lavatelli, Long, Snyder, and Williams, *ibid.* **72** (1947), 1147.

§ Hamermesh and Schwinger, *ibid.* **69** (1946), 145.

the interference effects are determined by

$$\{(s+1)a_{s+\frac{1}{2}} + sa_{s-\frac{1}{2}}\}^2(2s+1)^{-1}, \quad (83)$$

and may well be reduced to a negligible value by cancellation.

Fermi and Marshall† have carried out experiments to determine the relative signs of the scattered amplitudes or ‘scattering lengths’ for different nuclei by making use of certain interference phenomena. In the Bragg scattering of slow neutrons by crystals containing at least two kinds of atoms, the relative intensity of the scattering in different orders and crystalline planes depends on the phase relations between the waves scattered by the different atoms and hence on the relative signs of the scattering lengths. From such effects with hydrides the range of the neutron-proton interaction in the 3S state may be determined.‡

Similarly, the cross-section for scattering by a molecule, of neutrons with wave-length comparable with or greater than the atomic distances, depends on the relative sign of the scattering lengths due to each constituent nucleus. If the neutron mass is assumed to be negligible compared with that of the atoms concerned, the effects may be treated in the same way as the diffraction of X-rays by molecules.

A third method depends on observing the limiting angle for total reflection of neutrons from substances with positive scattering length (the same sign as for the 3S scattering of neutrons by protons, in which there is a phase change of π on scattering). For such substances the refractive index is less than unity, being given by

$$n = 1 - \lambda^2 N a / 2\pi,$$

where λ is the wave-length and N the number of atoms/c.c.

It is found that most nuclei have positive scattering lengths, exceptions being hydrogen (for the 1S scattering) and one or more isotopes of lithium and manganese.

The scattering of slow neutrons by crystals has been discussed in considerable detail by several authors.§ The technique involved is similar to that used for the corresponding problem for X-rays. We shall therefore not give any detailed discussion here. It is of interest to mention, however, that the use of the pseudo-potential for these problems may be extended to include absorption. This may be done by treating the scattering length a as complex. If Q_s , Q_a are the scattering

† *Phys. Rev.* **71** (1947), 666.

‡ Shull, etc., *ibid.* **73** (1948), 262 and 842.

§ Rasetti, *ibid.* **58** (1940), 321; Halpern, Hamermesh, and Johnson, *ibid.* **59** (1941), 981; Seiger and Teller, *ibid.* **62** (1942), 37; Weinstock, *ibid.* **65** (1944), 1; Goldberger and Seitz, *ibid.* **71** (1947), 294.

and absorption cross-sections respectively, then

$$a = \pm \left[\frac{Q_s}{4\pi} - \left(\frac{kQ_a}{4\pi} \right)^2 \right]^{\frac{1}{2}} + i \frac{kQ_a}{4\pi}, \quad (84)$$

where k is the neutron wave number.†

4. Magnetic scattering of slow neutrons‡

We now consider scattering effects due to interaction between the magnetic moment of the neutron and the spins of atomic electrons. These effects are specially important as they make possible the production of partially polarized neutron beams. By use of these beams and radio-frequency technique it has been possible to determine the magnetic moment of the neutron with great accuracy.§ It is possible also that the study of the scattering of neutrons by ferromagnetic materials may yield useful information about the internal structure of such bodies.

The scattering of a neutron by an atom, including magnetic effects, may be calculated by Born's approximation if a further term is added to the appropriate pseudo-potential to represent the magnetic interaction.

The energy of interaction of an electron of coordinate \mathbf{r} with a magnetic field of vector potential \mathbf{A} is given by $-\epsilon\boldsymbol{\alpha}\cdot\mathbf{A}(\mathbf{r})$, where $\boldsymbol{\alpha}$ is the vector matrix which occurs in Dirac's equations, $c\boldsymbol{\alpha}$ being the operator representing the electron velocity. If the vector potential arises from the magnetic field of a neutron of coordinate \mathbf{r}_n we have

$$\mathbf{A}(\mathbf{r}) = \nabla \left(\frac{1}{|\mathbf{r} - \mathbf{r}_n|} \right) \wedge \mathbf{M}_n, \quad (85)$$

where \mathbf{M}_n is the neutron magnetic moment. The magnetic interaction with the atomic electrons can therefore be written

$$\begin{aligned} V_{\text{mag}} &= \epsilon \sum_l \boldsymbol{\alpha}_l \cdot \nabla_n \left(\frac{1}{|\mathbf{r}_l - \mathbf{r}_n|} \right) \wedge \mathbf{M}_n, \\ &= \epsilon \mathbf{M}_n \cdot \sum_l \boldsymbol{\alpha}_l \wedge \nabla_n \left(\frac{1}{|\mathbf{r}_l - \mathbf{r}_n|} \right), \\ &= \epsilon \mu_n \boldsymbol{\sigma}_n \cdot \sum_l \boldsymbol{\alpha}_l \wedge \nabla_n \left(\frac{1}{|\mathbf{r}_l - \mathbf{r}_n|} \right), \end{aligned} \quad (86)$$

† This result follows from the relation $a = \lim_{k \rightarrow 0} \left\{ \frac{1}{2ik} (e^{2i\eta} - 1) \right\}$ with the phase η taken as complex and related to Q_s and Q_a as in the formulae (6) and (7) of Chapter VIII.

‡ Bloch, *Phys. Rev.* **50** (1936), 259; Halpern and Johnson, *ibid.* **51** (1937), 992; **52** (1937), 52; **55** (1939), 89; Schwinger, *ibid.* **51** (1937), 544.

§ Arnold and Roberts, *ibid.* **71** (1947), 878.

the suffix l distinguishing the various electrons. The neutron moment has been written in the form $\mu_n \sigma_n$, where σ_n is the spin operator and μ_n the magnitude of the moment.

In a ferromagnetic substance, magnetized to saturation, the spins of the electrons responsible for the ferromagnetic properties are strongly coupled and aligned parallel to the direction of magnetization. Slow neutrons are insufficiently energetic to reverse the spins of any of these electrons, so the scattering is entirely elastic. The contribution to the scattered amplitude due to V_{mag} is therefore given, by Born's approximation, as

$$f_m(\theta, \phi) = \frac{2\pi M \epsilon \mu_n}{\hbar^2} \sum_{\text{spin}} \chi_n \sigma_n \chi_n^* \cdot \sum_l \int \exp\{ik(\mathbf{n}_0 - \mathbf{n}_1) \cdot \mathbf{r}_n\} \mathbf{P}_l d\tau_n d\tau_l,$$

where
$$\mathbf{P}_l = \Psi_A'(\mathbf{r}_l) \nabla_n \left(\frac{1}{|\mathbf{r}_l - \mathbf{r}_n|} \right) \wedge \alpha_l \Psi_A'^*(\mathbf{r}_l). \tag{87}$$

In this expression χ_n represents the neutron spin function. Ψ_A' is the wave function of the atomic electrons including their spin, and the integration over $d\tau_l$ is also supposed to include summation over the spin coordinates. \mathbf{n}_0 and \mathbf{n}_1 are unit vectors in the direction of incidence and of scattering respectively, k is the neutron wave number, and M its mass.

Since the neutron spin is unchanged, $\sum_{\text{spin}} \chi_n \sigma_n \chi_n^*$ can be replaced by the unit vector \mathbf{s}_n in the direction of the neutron spin. Furthermore, in non-relativistic approximation, the contribution to α_l from electron spin is such that†

$$\Psi_A'(\mathbf{r}_l) \alpha_l \Psi_A'^*(\mathbf{r}_l) \simeq \frac{\hbar}{mc} \text{curl}_l(\Psi_A' \sigma_l \Psi_A'^*), \tag{88}$$

where σ_l is the Pauli spin operator for the l th electron and m is the electron mass.

The electrons which contribute to the ferromagnetism will have their spins aligned in the direction of magnetization. Since there is no reversal of electron spin during the collision, the summation over the spin coordinates of each of these electrons gives

$$\sum_{\text{spin}} \Psi_A' \sigma_l \Psi_A'^* = \psi_A \mathbf{s} \psi_A^*, \tag{89}$$

where \mathbf{s} is a unit vector in the direction of magnetization and the functions ψ_A involve only the space coordinates of the electrons. The remaining atomic electrons will not contribute anything to the spin summation on the average.

† W. Pauli, *Handbuch der Physik*, 24 A (1933), 238.

We therefore have, on changing the variables from $\mathbf{r}_n, \mathbf{r}_l$ to \mathbf{r}, \mathbf{r}_l , where $\mathbf{r} = \mathbf{r}_n - \mathbf{r}_l$, and carrying out the summation over the atomic electrons,

$$f_m(\theta, \phi) = \frac{M\epsilon}{m\hbar c} S\mu_n \mathbf{s}_n \cdot \int \exp(iK\mathbf{n} \cdot \mathbf{r}) \nabla \left(\frac{1}{r} \right) \wedge \mathbf{G} d\tau,$$

where
$$\mathbf{G} = \mathbf{s} \wedge \int \nabla (|\psi_m|^2) \exp(iK\mathbf{n} \cdot \mathbf{r}_l) d\tau_l, \quad (90)$$

S being the total electron spin quantum number and $|\psi_m|^2$ the charge density of the electrons responsible for the ferromagnetic properties (presumably the $3d$ electrons) in terms of a single electronic coordinate \mathbf{r}_l . Here we have written

$$k(\mathbf{n}_0 - \mathbf{n}_1) = 2k \sin \frac{1}{2}\theta \mathbf{n} = K\mathbf{n},$$

where \mathbf{n} is a unit vector.

Following the same procedure to ensure convergence as in Chap. VII, § 1, we have

$$\begin{aligned} \int \exp(iK\mathbf{n} \cdot \mathbf{r}) \nabla \left(\frac{1}{r} \right) d\tau &= \int \nabla \{ \exp(iK\mathbf{n} \cdot \mathbf{r}) \} \frac{d\tau}{r} \\ &= iK\mathbf{n} \int \exp(iK\mathbf{n} \cdot \mathbf{r}) \frac{d\tau}{r} \\ &= \frac{4\pi i}{K} \mathbf{n}, \end{aligned} \quad (91)$$

and similarly

$$\begin{aligned} \int \nabla_l (|\psi_m|^2) \exp(iK\mathbf{n} \cdot \mathbf{r}_l) d\tau_l &= iK\mathbf{n} \int |\psi_m|^2 \exp(iK\mathbf{n} \cdot \mathbf{r}_l) d\tau_l \\ &= iK\mathbf{n}F, \quad \text{say.} \end{aligned} \quad (92)$$

This gives

$$\begin{aligned} f_m(\theta, \phi) &= \frac{2M\epsilon}{m\hbar c} S\mu_n F \mathbf{s}_n \cdot \{ \mathbf{n} \wedge (\mathbf{n} \wedge \mathbf{s}) \} \\ &= \frac{2M\epsilon}{m\hbar c} S\mu_n F (\mathbf{s}_n \cdot \mathbf{n} \mathbf{n} \cdot \mathbf{s} - \mathbf{s}_n \cdot \mathbf{s}) \\ &= \frac{\epsilon^2}{mc^2} \gamma_n S F \mathbf{s}_n \cdot \mathbf{q}, \end{aligned} \quad (93)$$

where γ_n is the neutron magnetic moment in nuclear magnetons and \mathbf{q} is the vector $\mathbf{n} \cdot \mathbf{s} \mathbf{n} - \mathbf{s}$.

The total scattered amplitude, including the nuclear scattering, will be

$$a + f_m(\theta, \phi), \quad (94)$$

where a is the scattering length for the particular nucleus. This assumes that the neutron beam is completely polarized with spin parallel to \mathbf{s}_n .

Normally the beam will be unpolarized and the scattered amplitude must be written

$$a \pm f_m(\theta, \phi), \quad (95)$$

to allow for the two possible spin orientations. Since the cross-section for scattering depends on the neutron spin, polarization effects can be produced by scattering from magnetized iron.

Although f_m is not negligible, its contribution to the total cross-section is rather smaller than $4\pi a^2$. Taking ϵ^2/mc^2 as 2.8×10^{-13} cm., $\gamma = 1.9$, $S = 5/2$, and the mean value of F as about 0.1, for thermal neutrons, the mean value of $f_m(\theta, \phi)$ comes out to be 1.3×10^{-13} cm. as compared with the value 8×10^{-13} cm. for a , for iron.† We may therefore write approximately for the scattering cross-section

$$Q_0 \pm p, \quad \text{where} \quad Q_0 = 4\pi a^2, \quad p = \frac{2\epsilon^2}{mc^2} \gamma_n Sa \int_0^\pi \int_0^{2\pi} F \mathbf{s}_n \cdot \mathbf{q} \sin \theta \, d\theta d\phi. \quad (96)$$

The form factor F is exactly similar to the atom form factor discussed in Chap. VII, § 1, except that the only electrons which contribute to it are those which are responsible for the ferromagnetism, presumably the $3d$ electrons.

The existence of the term p may be verified by observing the transmission of a collimated beam of neutrons of intensity I_0 through a block of iron. If the iron is unmagnetized the intensity I of the beam after passing through a thickness l of the block will be given by

$$I = I_0 \exp(-NlQ_0), \quad (97)$$

where N is the number of atoms per c.c. If now the iron is magnetized to saturation the transmitted intensity will be

$$I + \Delta I = \frac{1}{2} I_0 [\exp\{-Nl(Q_0 + p)\} + \exp\{-Nl(Q_0 - p)\}], \quad (98)$$

giving a relative increase in transmitted intensity

$$\begin{aligned} \frac{\Delta I}{I} &= \cosh(Nlp) - 1 \\ &\simeq \frac{1}{2} N^2 p^2 l^2. \end{aligned} \quad (99)$$

Under these geometrical conditions

$$p = \frac{2\pi\epsilon^2\gamma_n}{mc^2} Sa \int_0^\pi F(\theta)(1 + \cos^2 \theta) \sin \theta \, d\theta. \quad (100)$$

Although this result is valid with perfect saturation, small departures

† Fermi and Marshall, *Phys. Rev.* 71 (1947), 666.

from that condition lead to a considerable reduction in the effect. This is due to depolarization of the neutrons in making the non-adiabatic passage from one domain in the iron to the next in which the magnetization is slightly different. Halpern and Holstein† have considered this effect and shown that it introduces a factor $f\{\lambda/(\epsilon l)\}$ into the expression (99) for $\Delta I/I$, λ being a quantity related to the linear dimensions of the domains in the magnet, ϵ the percentage deviation from complete saturation, and

$$f(x) = 2x^2\{e^{-1/x} + (1/x) - 1\}. \quad (101)$$

Experimental verification of these transmission effects has been found by Bloch and Staub and their collaborators.‡ The absolute value of p is difficult to predict accurately as the density distribution of the $3d$ electrons of iron is not known with accuracy—the observed value is between 2.2 and 2.3×10^{-24} cm.² In a magnetizing field of 10,000 gauss, $\Delta I/I$ should be about 22.5 per cent. This corresponds to a degree of polarization, measured by

$$\delta = \left| \frac{I^+ - I^-}{I^+ + I^-} \right|, \quad (102)$$

of as much as 60 per cent., I^+ , I^- referring to the transmitted intensities of beams with spins respectively parallel and antiparallel to the direction of magnetization.

The preparation of partially polarized neutron beams is of great importance as an essential part of the technique involved in measuring with precision the magnetic moment of the neutron.§

The magnetic scattering by a ferromagnet is a relatively simple problem as only the elastic scattering need be considered. A discussion of other possibilities has been given by Halpern and Johnson,|| who also considered various polarization phenomena which might arise.

5. Collisions of fast particles with medium to heavy nuclei

As the level spacing in the excited complex formed by capture of a nucleon (or deuteron, α -particle, or other light nucleus) by a medium or heavy nucleus is at most of order 10 e.V., it is not possible to distinguish resonance effects in the collisions of energetic particles with such nuclei. Indeed, it may well occur that the state of the complex

† *Phys. Rev.* **59** (1941), 960.

‡ Bloch, Hammermesh, and Staub, *ibid.* **64** (1943), 47; Bloch, Condit, and Staub, *ibid.* **70** (1946), 972. See also Hughes, Wallace, and Holtzmann, *ibid.* **73** (1948), 1277.

§ Alvarez and Bloch, *ibid.* **57** (1940), 111; **57** (1940), 352; Arnold and Roberts, *ibid.* **71** (1947), 878.

|| *Ibid.* **55** (1939), 898; see also van Vleck, *ibid.* **55** (1939), 924.

formed lies in the region of overlapping levels. All that can be observed in the cross-section for a particular process will be an average over an energy interval containing many levels. We may therefore use the formulae of Chap. VIII, § 8.3.

We first consider the collisions of medium to fast neutrons (1 k.e.V. to 10 M.e.V. say), as the formation of the complex is not then influenced by any barrier penetration effects. If the cross-section for formation of the complex is given by Q_n^c , the cross-section for a process in which a particle P is emitted will be given by

$$Q^P = Q_n^c \frac{\Gamma_P}{\Gamma}, \tag{103}$$

where $\Gamma = \sum \Gamma_P$. Γ_P is the suitably averaged partial width for emission of the particle P . Included among the possibilities will be emission of γ -radiation (partial width Γ_γ) and re-emission of the neutron with its initial energy (partial width Γ_n^{el}). Further, if k is the neutron wave-number

$$Q_n^c = \frac{2\pi^2}{k^2} \frac{\Gamma_n^{el}}{D} \quad (kR \ll 1), \tag{104 a}$$

$$= \pi R^2 \quad (kR \gg 1), \tag{104 b}$$

where D is the level spacing about the excited level of the complex which is formed and R is the nuclear radius. For intermediate values of kR it is convenient to write Q_n^c in the form $\pi R^2 \xi$, where ξ is the 'sticking probability'.

Owing to the high Coulomb potential barrier, the emission of charged particles from the complex is usually very improbable except for the heavier nuclei such as U235 which, in their ground states, are already unstable towards α -particle emission and/or fission. Excluding such cases for the present we may write

$$\Gamma = \Gamma_\gamma + \Gamma_n^{el} + \Gamma_n^{in}, \tag{105}$$

where Γ_n^{in} is the contribution to the total width due to emission of a neutron with less than its initial energy, i.e. an inelastic collision.

If the neutron energy is not enough to excite the lowest excited state of the nucleus ($\simeq 100,000$ e.V. for the heavy radioactive nuclei), $\Gamma_n^{in} = 0$ and only radiative capture or elastic scattering can occur. From the experimental data discussed in § 2.22 it appears that, for nuclei of medium mass,

$$\Gamma_n^{el} \simeq 1.4E^{\frac{1}{2}} \times 10^{-3} \text{ e.V.}, \tag{106}$$

where E is the neutron energy in electron volts. Γ_γ is of the order 0.1 e.V. for complexes formed by thermal capture and is not likely to change

much with neutron energy. We see therefore that, when the neutron energy exceeds 5,000 e.V. or so, the cross-section for capture falls below that for elastic scattering. At such energies (104a) is applicable, so, taking D as of the order 10 e.V. as in § 2.2, we have

$$Q^r \simeq \frac{h^2}{4mE} \frac{\Gamma_r}{D} \simeq 0.8 \times 10^{-24} \text{ cm.}^2 \quad \text{for } E = 5 \text{ k.e.V.}$$

As the neutron energy becomes adequate to produce excitation Γ_n^{in}

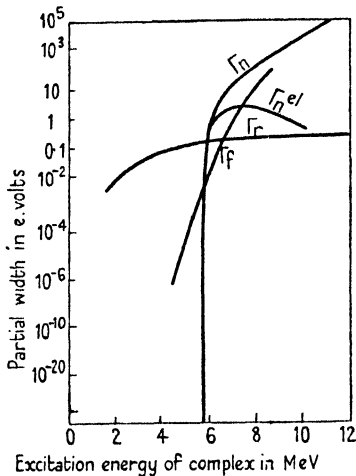


FIG. 69. Schematic diagram of the variation of the partial level widths Γ_r , Γ_f , Γ_n , Γ_n^{el} with excitation energy of a heavy compound nucleus.

becomes important and soon exceeds Γ_n . The partial width for emission of a neutron, leaving the residual nucleus with an excitation energy U e.V., will at first be of the order $1.4 \times 10^{-3}(E-U)^{\frac{1}{2}}$ e.V. The number of such excited states increases rapidly with the available energy, so the sum of the contributions from each soon exceeds Γ_n^{el} . When many levels may be excited the statistical formulae of Chap. VIII, § 8.32, apply. Γ_n^{in} is then of the order DN , where N is the number of excited levels in which the residual nucleus may be left after neutron emission, whereas Γ_n^{el} is of order D . Furthermore, the relative probability of leaving the nucleus with a particular energy of excitation is proportional to the level density in that region. It is therefore most likely that the nucleus will be left in a highly excited state—most neutrons will be emitted with low energy (see Chap. VIII, § 8.32). Typical behaviour of Γ_r , Γ_n^{el} , and Γ_n^{in} for a heavy nucleus is illustrated in Fig. 69.

These general conclusions are in agreement with observation, though no very detailed series of measurements have yet been carried out in the energy range concerned.†

These general conclusions are in agreement with observation, though no very detailed series of measurements have yet been carried out in the energy range concerned.†

If we now turn to effects produced by charged particles, the same general considerations apply to the relative probabilities of different modes of break-up of the complex, once formed. Thus a fast charged particle is most likely to produce a disintegration in which a low energy neutron is emitted. This is true, even if the excitation energy of the complex produced by capture of the charged particle is so great that

† See, however, Szilard, Bernstein, Feld, and Ashkin, *Phys. Rev.* **73** (1948), 1307.

a charged particle of one or more kinds may be emitted with sufficient energy to pass over the barrier. Owing to the high internal energy of the deuteron this may often be possible in capture of such nuclei with a few M.e.V. energy. Thus, if B is the barrier height and E_P the energy released in emitting the charged particle P , leaving the residual nucleus in its ground state, the only levels of this latter nucleus which are effectively accessible as final levels after emission of P are those which lie within an energy range $E_P - B$ of the ground level. For neutron emission the corresponding range will be E_n . As E_n will be comparable with E_P , it will be much greater than $E_P - B$. Since the total width for emission of a particular particle is roughly proportional to the number of accessible final levels of the residual nucleus, and as this number increases exponentially with the energy range above the ground state (see § 2.1), it is clear that neutron emission will normally remain the most important process.

Among charged particles all of which may be sufficiently energetic to pass over the barrier, that one for which $E_P - B$ is largest will have the greatest probability of emission. If none can pass over, the relative probability is determined by the combined effect of the barrier penetration and the number of available final levels. Thus, emission of an α -particle may often occur with comparable probability to that of a proton—the smaller barrier penetration is compensated by the great number of available final states due to the low internal energy of the α -particle. On the other hand, the high internal energy of the deuteron restricts the number of final states to such an extent that a deuteron is rarely emitted from a complex.

The cross-section Q_P^c for formation of a complex by capture of a charged particle P differs from the corresponding cross-section Q_n^c for formation by neutron capture, mainly through the effect of the barrier. If the incident particle has a wave-length considerably greater than nuclear dimensions, then Q_P^c is given by a formula similar to (104 a), but Γ_P^{el} differs from Γ_n^{el} by inclusion of the penetration probability e^{-P} for particles of zero angular momentum viz.:

$$\Gamma_P^{\text{el}} \simeq \Gamma_n^{\text{el}} e^{-P}. \quad (107)$$

A further factor, less than unity, must be introduced when the incident particle is not a simple nucleon. This allows for the necessity for satisfying orientation conditions before the complex can form, an effect which does not seem to be very important even for α -particles.

When the incident particle has a wave-length shorter than the nuclear

radius we have, referring to the derivation of (104 b) in Chap. VIII, §8.31,

$$Q_P^a = \frac{\pi}{k^2} \sum (2l+1) \zeta_l e^{-P_l}, \quad (108)$$

where e^{-P_l} is the penetration probability and ζ_l the sticking probability, for particles with l quantum units of angular momentum. If ζ_l can be taken as unity for all l for which e^{-P_l} is appreciable, we then have in place of (108)

$$Q_P^a = \pi l_c^2 / k^2, \quad (109)$$

where

$$l_c^2 = \sum (2l+1) e^{-P_l}. \quad (110)$$

For any particular case l_c may be calculated from the formula (36) of Chapter III. If the sticking probability is less than unity by an appreciable factor it will usually be sufficient to write

$$Q_P^c = \frac{\pi l_c^2}{k^2} \bar{\zeta}, \quad (111)$$

where $\bar{\zeta}$ is, apart from an orientation factor, practically the same as for neutrons of the same velocity.

Disintegration of heavy nuclei by deuteron impact presents a special case inasmuch as its exceptionally low binding energy makes it possible for the deuteron to be broken up before the proton has completely penetrated the potential barrier. The neutron may then be absorbed and the proton ejected. This possibility was first suggested by Oppenheimer and Phillips† and discussed subsequently by several authors.‡ It appears that, while the process is unimportant for light nuclei, it is responsible for the relatively large cross-sections for disintegration of heavy nuclei by deuteron impact.

6. Nuclear fission

The binding energy of a nucleus, per nuclear particle, reaches a maximum for nuclei with atomic mass near that of nickel and then decreases again with increasing mass number. It follows that a nucleus such as uranium is energetically highly unstable towards division into two lighter nuclei of comparable atomic mass, i.e. nuclear fission. The probability of such fission is normally very low because of the high energy of the activated configuration through which the system must pass in order to divide. In the case of the U235 nucleus the capture of a slow neutron leads to a U236 complex which already possesses excita-

† *Phys. Rev.* **48** (1935), 500.

‡ Kapur, *Proc. Roy. Soc. A*, **163** (1937), 553; *Ind. J. Phys.* **13** (1939), 87; Kapur and Peierls, *Proc. Roy. Soc. A*, **163** (1937), 606; Lifshitz, *Phys. Zeit. d. Sow. Un.* **13** (1938), 324; Bethe, *Phys. Rev.* **53** (1938), 34; Volkoff, *ibid.* **57** (1940), 866.

tion energy in excess of that required to pass through the activated state—the neutron binding energy is greater than the activation energy. There is therefore an appreciable probability that the complex will break up in this way instead of getting rid of the surplus energy by γ -radiation or neutron re-emission. For no other nucleus, which occurs naturally in appreciable quantity, does capture of a thermal neutron lead to a complex with energy exceeding that of the activated state for fission. Neutrons with kinetic energy of the order of 0.5 or more M.e.V. can, however, produce such superactivated complexes on collision with certain other nuclei—in particular with U238 and Th232.

The occurrence of nuclear fission was first indicated by the discovery by Hahn and Strassmann in 1939,† of products with the chemical properties of barium from the reaction of slow neutrons with uranium. The mechanism responsible was suggested shortly afterwards by Meitner and Frisch‡ and a detailed theoretical discussion followed in a now classic paper by Bohr and Wheeler.§ Although experimental results were only available using natural uranium, the latter authors were able, from theoretical arguments, to deduce which isotopes were responsible for the different effects. As the methods they employed provide an excellent illustration of the application of nuclear collision theory, we shall briefly outline them here.

The experimental information available was as follows:

(a) Resonance capture followed by radiation|| occurs for neutrons with energies in the neighbourhood of 25 e.V., the cross-section being 1.2×10^{-21} cm.², averaged over the resonance region.

(b) The absorption cross-section for these neutrons measured by the method of self-indication, is 1.2×10^{-21} cm.² This cross-section Q_g is related to the cross-section at exact resonance, Q_{res} , by††

$$Q_g = \frac{1}{2} Q_{\text{res}} f\left(\frac{\Gamma}{\Delta}\right), \quad (112)$$

where Δ is the Doppler width and Γ the true width of the resonance level. The function f reduces to unity when $\Gamma \gg \Delta$ and equals $\frac{1}{2}\pi^{\frac{1}{2}}\Delta/\Gamma$ when $\Delta \ll \Gamma$. We therefore have:

$$\begin{aligned} \text{Maximum cross-section} &= 2.4 \times 10^{-21} \text{ cm.}^2 & (\Delta \ll \Gamma), \\ &= 3.0 \times 10^{-21} \Delta/\Gamma \text{ cm.}^2 & (\Delta \gg \Gamma). \end{aligned} \quad (113)$$

For uranium $\Delta = 0.12$ e.V.

† *Naturwiss.* 27 (1939), 11. ‡ *Nature*, 143 (1939), 239. § *Phys. Rev.* 56 (1939), 426.

|| The observed result was the production of β -activity but not of any elements other than uranium, in contrast with the effects produced by thermal and by fast neutrons.

†† Bethe, *Rev. Mod. Phys.* 9 (1937), 140.

(c) For radiative capture of thermal neutrons the cross-section is 1.2×10^{-24} cm.²

(d) In the resonance range the fission cross-section is < 0.1 of that for radiative capture.

(e) Thermal neutrons produce fission, the cross-section being between 2 and 3×10^{-24} cm.²

(f) The cross-section for fission by slow neutrons varies as v^{-1} up to energies of a few e.V. at least, v^{-1} being the neutron velocity.

(g) Neutrons with energy between 2 and 3 M.e.V. also produce fission, the cross-section being about 0.5×10^{-24} cm.² and varying only slightly over this energy range.

6.1. Resonant radiative capture

Natural uranium is a mixture of three isotopes, U238, U235, and U234 with abundance ratio 1:1/139:1/17,000. The maximum cross-section, π/k^2 , for capture of a 25 e.V. neutron is 2.5×10^{-20} cm.² It follows from (b) that only the abundant isotope can be responsible for the radiative capture. By following an exactly similar analysis to that used in § 2.22 it follows that Γ_n , the partial neutron width, is equal to $\Gamma_r/40 \simeq \Gamma/40$ or to $\Delta/40$ according as $\Gamma \gg \Delta$ or $\ll \Delta$ respectively. Since Δ is 0.12 e.V. it follows that $\Gamma_n \geq 0.003$ e.V. From the analysis of data for capture of nuclei of medium atomic mass Γ_n would be expected to be of order 0.01 e.V. (i.e. $1.4 \times 10^{-3} \times 25^{\frac{1}{2}}$) for a resonance energy of 25 e.V. As it should be smaller rather than larger for a heavy nucleus such as uranium, Γ_n may be taken as $\simeq 0.003$ e.V. Γ_r cannot then be greater than 0.12 e.V., but is probably not much smaller as judged from experiments with lighter nuclei.

With the estimated values for Γ_n and Γ_r the cross-section for radiative capture of thermal neutrons can be derived if only the one resonance level is responsible. Thus

$$Q_r(\text{thermal}) = (\pi/k^2) \Gamma_n(\text{thermal}) \Gamma_r/E_R^2. \quad (114)$$

As Γ_n is proportional to the neutron velocity, $\Gamma_n(\text{thermal})$ may be obtained, giving

$$Q_r(\text{thermal}) \simeq 0.4 \times 10^{-24} \text{ cm.}^2 \quad (115)$$

Referring to (c) it will be seen that this value is roughly $\frac{1}{3}$ of the observed, suggesting that more than one level is responsible. Allowing for the influence of levels both above and below thermal energies, the factor 3 suggests that the level spacing D , in the U239 complex, is of the same order as the observed resonance energy, about 20 e.V.

6.2. Slow neutron fission

Turning now to fission by slow neutrons it is easily seen that it cannot be due to the abundant isotope. From (d) it follows that the partial width for fission is $< \frac{1}{10}\Gamma_f$, at the resonance level. As Γ_f will decrease, if anything, with the neutron energy (see § 6.3 below) it follows from (c) that the cross-section for fission of U238 by slow neutrons is $< 1.2 \times 10^{-25}$ cm.², over 20 times smaller than the value observed for natural uranium.

The fission cross-section Q_f for thermal neutrons must therefore be between 3 and 4×10^{-22} cm.², or between 3 and 4×10^{-20} cm.², according as it is due to U235 or U234 respectively. Two possibilities must now be considered—either the excited complex lies in the region of separated or overlapping levels.

In the former case the effect is principally due to a single resonance level and

$$Q_f = \frac{\pi}{k^2} \left(1 \pm \frac{1}{2s+1} \right) \frac{\Gamma_n \Gamma_f}{(E - E_R)^2 + \frac{1}{4}\Gamma^2} \quad (116)$$

in the usual notation, Γ_f being the width due to fission. Γ_n should be nearly the same for all three isotopes, so it may again be taken as 10^{-4} e.V. for thermal neutrons. In order that (f) be satisfied either E_R or $\frac{1}{2}\Gamma$ or both must be greater than a few e.V. Substituting numerical values and remembering that $\Gamma > \Gamma_f$, it is found that, if U234 is the isotope responsible, both Γ and E_R must be much smaller than 1 e.V. (taking $s = 0$ and the upper sign in (116), $\Gamma \leq 4/17$ e.V. and $|E_R| < 2/17$ e.V.). This possibility may therefore be excluded.

No such contradiction appears if the effect may be ascribed to U235. For different assumptions as to the spins it is then found that: (i) for $s \geq \frac{3}{2}$, $\Gamma < 13$ e.V., $|E_R| < 3$ e.V.; (ii) for $s = \frac{1}{2}$, and the lower sign $\Gamma < 7$ e.V., $|E_R| < 1.7$ e.V.; (iii) for $s = \frac{1}{2}$ and the upper sign, $\Gamma < 20$ e.V., $|E_R| < 5$ e.V. Further, since either $|E_R|$ or $\frac{1}{2}\Gamma$ must be 1 e.V. or greater,

$$\Gamma_f > 10 \text{ e.V.}$$

There is no inconsistency here except possibly if the conditions (ii) apply. On the other hand, Γ_f must be of the order of the level spacing, which, as estimated from the radiative capture, is about 20 e.V. for the excited complex formed from U238. No difference in order of magnitude would be expected for U235. It is therefore necessary to consider the further possibility, that the excited complex falls in the region of overlapping levels. In that case, we have

$$Q_f = \frac{2\pi^2 \Gamma_n}{k^2 D}. \quad (117)$$

This is satisfied for U235 with $D = 20$ e.V., but for U234 to be responsible D would have to have the impossibly small value of 0.4 e.V.

It may then be concluded that the slow neutron fission is due to U235, from which a complex excited to the region of overlapping levels is formed. However, the possibility that the effect arises from a single isolated level cannot be ruled out on the basis of the data listed above. In either case the fission width Γ_f must be at least of the order 10 e.V.

6.3. Theoretical estimate of fission width

As a further check on the validity of these arguments it is of interest to consider what value Γ_f might be expected to have. Fission involves the relative motion of two heavy, slow nuclear fragments, so classical arguments may be applied. In particular, the transition state method (Chap. VIII, § 8.4) may be employed. The problem is the one discussed in § 8.4; and we have

$$\Gamma_f = \frac{D}{2\pi} N^*, \quad (118)$$

where N^* is the number of levels available in the transition state through which the configuration of the system must pass in order to divide. If we assume that the level distribution in the transition state is similar to that for a normal nucleus, N^* is likely to be of order unity when the compound nucleus formed by slow neutron capture has an energy greater than that necessary to carry the system over the transition pass by 50 to 100 k.e.V. A value of Γ_f comparable with 10 e.V. is therefore quite reasonable.

6.4. Fast neutron fission

It remains to consider the fission by fast neutrons. This cannot be due to either of the rare isotopes. At the energies concerned the neutron wave-length is small compared with the nuclear radius (9.5×10^{-13} cm. for U). The capture cross-section cannot then be appreciably greater than πR^2 (Chap. VIII, § 1) whereas, even if U235 were responsible, it would have a cross-section (see (*g*) above) as large as 7×10^{-23} cm.², 25 times greater than the maximum.

No difficulty arises in associating the fast neutron effect with U238. As we are certainly concerned with the case of overlapping levels

$$\begin{aligned} Q_f &\simeq \pi R^2 \frac{\Gamma_f/D}{\Gamma_f/D + \Gamma_n/D}, \\ &= 2.8 \times 10^{-24} \frac{\Gamma_f/D}{\Gamma_f/D + \Gamma_n/D} \text{ cm.}^2 \end{aligned} \quad (119)$$

Γ_n/D is equal, on the average, to N_n , the number of levels in the U238 nucleus which may be excited by a fast neutron. It will increase rapidly with the excitation energy of the U239 complex formed, i.e. with the neutron energy. In a similar way Γ_f/D will increase rapidly with neutron energy from a zero value when the excitation energy of the U239 complex is less than the activation energy for fission. As the ground level from which N^* is reckoned lies higher than that for N_n , Γ_n will normally be greater than Γ_f , though it will vary with neutron energy in much the same way when the excitation energy is considerably in excess of that required for fission activation. This is consistent with (g) which requires $\Gamma_f/\Gamma_n \simeq \frac{1}{5}$. The energy variation of the fast neutron fission, referred to in (g) above, indicates that the activation energy for fission of U238 is less than 2 M.e.V. above the neutron binding energy.

Fig. 69 illustrates the way in which the different partial level widths Γ_f , Γ_n^{el} , Γ_n , Γ_r vary with the excitation energy of the compound nucleus, based on the above and preceding discussions of neutron capture phenomena.

These various conclusions have been justified by further experiments, even though the numerical values may have been altered in detail. Bohr and Wheeler were not only able to interpret the observations in the manner described above, but also showed that, if the current semi-empirical formulae for nuclear energies were used, the activation energy for fission of U236 should indeed be less than, and that for U239 greater than, the neutron binding energy. They also made predictions as to the fissile properties of other heavy nuclei.

References to recent work on analysis of high energy collisions between neutrons and protons (see footnote p. 302):—

‡ Camac and Bethe, *Phys. Rev.* **73** (1948), 191; Eisenstein and Rohrlich, *ibid.* 641; Ashkin and Wu, *ibid.* 973; Wu, *ibid.* 1132; Massey, Burhop, and Hu, *ibid.* 1403; Burhop and Yadav, *Nature* **162** (1948), 738; Chew and Goldberger, *Phys. Rev.* **73** (1948), 1409; Holmberg, *Kungl. Fysio. Sällskapetets i Lund Förhand.* **18** (1948), 1.

XIV

TRANSITION PROBABILITIES BY METHOD OF VARIATION OF PARAMETERS

1. Introduction

THE problems of quantum mechanics may conveniently be divided into two classes: the calculation of the eigenvalues of the energy and of the other observables of a dynamical system; and the calculation of the probability that a system will make a transition from one state to another under a given perturbation. Our aim in this chapter is to summarize the methods available for the solution of the latter class of problem. The previous chapters have been mainly concerned with the calculation of a particular type of transition probability, namely, that between two states of equal unquantized energy, due to a perturbation (interaction between atom and colliding particle) which is *not* a function of the time. For this type of problem we have found it convenient to use a periodic wave function, containing the time in the exponential factor $\exp(-2\pi i Wt/h)$ only. In this chapter we consider methods for the calculation of transition probabilities between states one of which is quantized; for such problems a periodic wave function cannot be used, and the 'Method of Variation of Parameters' must be employed.†

The transition probabilities calculated in this chapter may be divided into two classes in the following way:

I. Transitions, due to a perturbing field which is not a function of the time, from a quantized state to an unquantized state of equal energy. Examples of this kind of problem are: Gamow's theory of radioactive decay;‡ the Auger effect;§ the spontaneous dissociation of a molecule in a high rotational state. Perturbation theory is particularly suitable for the solution of this kind of problem, because, if the perturbing field is not 'small', it is impossible to use the conception of a transition probability. This may be seen most easily by reference to the Auger effect, where one has to calculate the probability that if two electrons are in excited states in one atom, one of them will fall to the ground state, giving up its energy to the other electron, which is thereby ejected from the atom. The 'perturbing energy' is here the interaction potential energy of the two electrons; if this is not 'small', so that the

† The method was first given by Dirac, *Proc. Roy. Soc. A*, **114** (1929), 243.

‡ *Atomic Nuclei and Radioactivity*, Oxford, 1931, p. 30.

§ Auger, *J. Phys. Rad.* **6** (1925), 205.

probability is small of the transition taking place in a time equal to the period of the atom, then it is meaningless to speak of the electrons as being initially in definite stationary states.

This is *not* true of transitions between two unquantized states. For such problems the validity of the perturbation method depends on the quite different considerations discussed in Chap. VII, § 2, and elsewhere in this book.

II. Transitions due to a perturbing field which is a function of the time. Here the initial and final states may be of different energy. Both the initial and final states may be quantized or unquantized. Examples are: the excitation and ionization of an atom by collision with an α -particle, when the α -particle is treated as a moving centre of force; the absorption of radiation and the photoelectric effect, when the light wave is not treated as a quantized field.

Transitions under the heading I may be considered as a special case of II. We shall therefore consider transition probabilities in the following order:

Transitions caused by a perturbing function which is a function of the time:

- (a) Final state quantized.
- (b) Final state in range of continuous energies.

Transitions caused by a perturbing function which is a periodic function of the time.

Transitions caused by a perturbation independent of the time.

2. Excitation of an atom by a perturbation which is a function of the time

For simplicity we take for the unperturbed system a single electron moving in the field of an infinitely heavy nucleus. Let \mathbf{r} denote the coordinates of the electron, H the Hamiltonian of the unperturbed atom, and $\psi_s(\mathbf{r})$, W_s the wave functions (not functions of t) and energy values of the stationary states, satisfying the equation

$$(H - W_s)\psi_s = 0. \quad (1)$$

We suppose the system to be perturbed by an energy term $V(\mathbf{r}, t)$, and the atom to be initially ($t = t_0$) in the state $s = 0$, the wave function being therefore initially

$$\psi_0(\mathbf{r})\exp(-2\pi i W_0 t/h). \quad (2)$$

At any subsequent time let the wave function be $\Psi(\mathbf{r}, t)$; then Ψ may

be determined from the initial condition (2) and from the wave equation

$$-\frac{\hbar}{2\pi i} \frac{\partial \Psi}{\partial t} - H\Psi = V\Psi. \quad (3)$$

To interpret Ψ we expand it in the form

$$\Psi(\mathbf{r}, t) = \sum_s a_s(t) \psi_s(\mathbf{r}) \exp(-2\pi i W_s t / \hbar), \quad (4)$$

and make the assumption that $|a_s(t)|^2$ is equal to the probability that the atom is in the state s at time t (for quantized states; for unquantized states cf. § 2.1). We have therefore to calculate the coefficients $a_s(t)$. Substituting (4) in the *left-hand* side of (3), we obtain

$$-\frac{\hbar}{2\pi i} \sum_s \left[\frac{d}{dt} a_s(t) \right] \psi_s(\mathbf{r}) \exp(-2\pi i W_s t / \hbar),$$

which is therefore equal to $V\Psi$. Hence, if we multiply both sides of this equation by any one of the functions $\psi_s^*(\mathbf{r}) \exp(+2\pi i W_s t / \hbar)$ and integrate over all \mathbf{r} , we obtain

$$\frac{d}{dt} a_s(t) = -\frac{2\pi i}{\hbar} \exp(2\pi i W_s t / \hbar) \int \psi_s^*(\mathbf{r}) V(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r}. \quad (5)$$

Initially, at time $t = t_0$, all the a_s are zero, except for a_0 , which is equal to unity; hence, integrating (5), we obtain, if $s \neq 0$,

$$a_s(t) = -\frac{2\pi i}{\hbar} \int_{t_0}^t dt \left\{ \exp(2\pi i W_s t / \hbar) \int \psi_s^*(\mathbf{r}) V(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r} \right\}. \quad (6)$$

This equation is exact. It cannot, however, be used to evaluate a_s , since the right-hand side contains the unknown function Ψ . If, however, it is permissible to assume that during the perturbation $\Psi(\mathbf{r}, t)$ is only slightly different from its original form, we may replace Ψ by $\psi_0(\mathbf{r}) \exp(-2\pi i W_0 t / \hbar)$ in the right-hand side of (6), and write

$$a_s(t) = -\frac{2\pi i}{\hbar} \int_{t_0}^t V_{s0}(t) \exp\{2\pi i (W_s - W_0) t / \hbar\} dt, \quad (7)$$

where

$$V_{s0}(t) = \int \psi_s^*(\mathbf{r}) V(\mathbf{r}, t) \psi_0(\mathbf{r}) d\mathbf{r}. \quad (8)$$

It is permissible to make this approximation if the perturbing energy is 'small'. The significance of this statement depends on the type of perturbation under consideration. We consider first the perturbation due to a heavy charged particle of charge E passing the atom, the particle being treated as a moving centre of force.

If the nucleus of the atom is at the origin, and the position of the perturbing particle at time t is

$$\mathbf{R} = (X, Y, vt),$$

then

$$V(\mathbf{r}, t) = -\epsilon E/|\mathbf{R}-\mathbf{r}|. \quad (9)$$

The probability that the atom will be left in the state s after the collision is $|a_s(\infty)|^2$, where

$$a_s(\infty) = -\frac{2\pi i}{h} \int_{-\infty}^{+\infty} V_{s0}(t) \exp[2\pi i(W_s - W_0)t/h] dt. \quad (10)$$

The perturbation method is valid here if the wave function is only slightly perturbed during the collision. This is obviously true for distant collisions, and may be shown to be true for collisions in which the particle passes through the atom, if its velocity is so great that the time during which the perturbation is effective is small. The method is also valid if the charge E on the particle is small compared with $Z\epsilon$. A *necessary* condition for the validity of the approximate method is

$$\sum_s |a_s(\infty)|^2 \ll 1.$$

The condition is not sufficient; for instance, for very slowly varying perturbations, $a_s(t)$ may be comparable with unity *during* the collision, even though $a_s(\infty)$ is small.†

If the perturbation is due to a light wave, we require to find the probability, $P_s \Delta t$, that the atom is excited to the state s in time Δt . Writing $\sum P_s = P$, the probability after time t that the atom remains in its normal state is then e^{-Pt} , it being of course assumed that spontaneous emission of radiation does not take place. The perturbation method will thus be valid for t such that

$$Pt = \sum_s |a_s(t)|^2 \ll 1.$$

Such perturbations are considered further in § 3, and it is shown that the method always gives an accurate value of P_s , unless the light wave is of intensity great enough to excite the atom in a time comparable with $1/\nu$, which is in practice never the case.

2.1. Ionization of an atom by a perturbation which is a function of the time

The wave function $\Psi(\mathbf{r}, t)$ describing the atom after the perturbation must contain terms which describe ionized states of the atom. The

† Cf. Chap. VIII, § 6.1.

expansion (3) is thus not complete; we must replace it by

$$\Psi(\mathbf{r}, t) = \sum a_s \psi_s \exp(-2\pi i W_s t/h) + \int a_W(t) \psi_W(\mathbf{r}) \exp(-2\pi i W t/h) dW, \quad (11)$$

where the functions $\psi_W(\mathbf{r})$ are the solutions of (1) for positive energy. These solutions are of the form

$$\psi_W(\mathbf{r}) = S_n^u(\theta, \phi) N L_{nW}(r),$$

where S_n^u is the normalized spherical harmonic given by

$$S_n^u = [(2n+1)(n-u)!/4\pi(n+u)!]^\dagger P_n^u(\cos \theta) e^{iu\phi},$$

and L is the radial part of the wave function normalized so that† [Chap. II, eq. (15)]

$$L \sim (kr)^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n)$$

and N is a constant. In (11) a summation over all values of n, u is to be understood. If we set

$$N = N(W) = 2k(hv)^{-\frac{1}{2}}, \quad (12)$$

then it may be shown‡ that the function G defined by

$$\int_0^R \psi_{Wnu}(\mathbf{r}) \psi_{W'nu}(\mathbf{r}) d\tau = G(W, R),$$

where the integration is over a sphere of radius R , has the following property: if $f(W)$ is any function of W , then

$$\lim_{R \rightarrow \infty} \int_0^R G(W, R) f(W) dW = f(W').$$

This property of the function $G(W, R)$ is conveniently expressed by the statement

$$G(W, \infty) = \delta(W - W'),$$

where δ is the 'δ-function' of Dirac.§

Making use of (12), it is easy to show that

$$a_W(t) = -\frac{2\pi i}{h} \int_{t_0}^t V_{W_0}(t) \exp[2\pi i(W - W_0)t/h] dt. \quad (13)$$

The wave function may be deduced from (11).

We shall now deduce from the wave function (11) the probability that the electron is ejected from the atom. We shall suppose that the perturbing function is operative only from time $t = 0$ to time $t = T$. We shall calculate the probability, $P dv_0 d\omega$, that, during this time interval, the electron is ejected in a direction lying in a solid angle $d\omega$

† The term $(2\pi Z e^2/hv) \log 2kr$ which occurs for Coulomb fields is omitted.

‡ Sommerfeld, *Wave Mechanics*, p. 290.

§ *Quantum Mechanics*, 3rd edition, p. 58.

about the direction given by the unit vector \mathbf{n} , and with velocity lying between $v_0, v_0 + dv_0$.

For this purpose we investigate the asymptotic form of $\Psi(\mathbf{r}, t)$ for values of \mathbf{r}, t given by $\mathbf{r} = \mathbf{n}v_0 t$ for values of the time t so long after the perturbation has ceased that

$$t dv_0 \gg T v_0.$$

Under these conditions it is clear that

$$\begin{aligned} P dv_0 d\omega &= |\Psi|^2 r^2 dr d\omega \\ &= |\Psi|^2 t^3 v_0^2 dv_0 d\omega. \end{aligned} \tag{14}$$

The right-hand side must be independent of t , and we shall show that this is the case.

We have then to investigate (11) for large r, t . The coefficient $a_{\mathcal{W}}(t)$ given by (13) tends to a constant value as $t \rightarrow \infty$, since the perturbing energy V is assumed to be finite only in the time interval $0 < t < T$. Replacing $\psi_{\mathcal{W}}(\mathbf{r})$ by its form for large r , we see that the only terms in the integral in (11) which involve r, t are

$$(kr)^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n) e^{-2\pi i W t / \hbar},$$

which may be written

$$\begin{aligned} (2ikr)^{-1} \left[\exp\left\{ \frac{2\pi i m}{\hbar} (vr - \frac{1}{2}v^2 t) - \frac{1}{2}n\pi i + i\eta_n \right\} - \right. \\ \left. - \exp\left\{ \frac{2\pi i m}{\hbar} (-vr - \frac{1}{2}v^2 t) + \frac{1}{2}n\pi i - i\eta_n \right\} \right]. \end{aligned} \tag{15}$$

The range of integration in (11) is from $W = 0$ to $W = \infty$, and hence from $v = 0$ to $v = \infty$. The first of the two terms in (15) has a stationary point† in this range, for $v = r/t$, and, for r, t sufficiently large, the whole integral comes from the neighbourhood of this point.† The second term in (15), which corresponds to an *ingoing* wave, has no such point in the range, and therefore makes a contribution to the integral of higher order in $1/t$. It may therefore be neglected.

The first term in (15) may be written

$$(2ikr)^{-1} \exp\left[\frac{2\pi i m}{\hbar} \left\{ -\frac{1}{2}t(v - v_0)^2 + (v_0 r - \frac{1}{2}v_0^2 t) - \frac{1}{2}n\pi i + i\eta_n \right\} \right], \tag{16}$$

where $v_0 = r/t$. Making use of the formula

$$\int_{-\infty}^{+\infty} \exp(iA\zeta^2) d\zeta = (\pi/iA)^{\frac{1}{2}} \quad (\zeta = v - v_0, \quad A = -\pi m t / \hbar),$$

† i.e. the function $e^{itf(v)}$ is said to have a stationary point for any value of v for which $f'(v) = 0$. The theorem quoted may easily be proved by deforming the path of integration into the complex plane.

we obtain from (11), putting $dW = mv dv$,

$$|\Psi| \sim \left| \sum_{n,u} a_{W_0 nu}(\infty) N(W_0) (2ik_0 r)^{-1} (h/mt)^{\frac{1}{2}} m v_0 \exp(-\frac{1}{2}n\pi i + i\eta_n) S_n^u(\theta, \phi) \right|,$$

where $W_0 = \frac{1}{2}mv_0^2$, etc.

This may be written

$$|\Psi| \sim r^{-1} (m v_0 / t)^{\frac{1}{2}} |f(\theta, \phi)|, \quad (17)$$

where $f(\theta, \phi) = (h/v_0)^{\frac{1}{2}} \sum_n \sum_u \exp(i\eta_n - \frac{1}{2}n\pi i) S_n^u(\theta, \phi) a_{W_0 nu}(\infty)$,

and where $r = v_0 t$. It will be seen that $|\Psi|^2$ is proportional to t^{-3} . From (14) we deduce that

$$P dv_0 d\omega = (m v_0^2 / h) |f(\theta, \phi)|^2 dv_0 d\omega. \quad (18)$$

Further, integrating over all θ, ϕ , we find that the total probability that a particle is ejected with energy between $W, W+dW$ is

$$\sum_n \sum_u |a_{W nu}(\infty)|^2 dW. \quad (19)$$

An alternative form may be given for $f(\theta, \phi)$. Inserting the formula (13) for a_W in (16) and referring to formulae Chap. II, (16), and Chap. VI, (24), we obtain

$$f(\theta, \phi) = \frac{2\pi m}{\hbar^2} \int d\tau' \int_{-\infty}^{+\infty} dt \mathfrak{F}(r', \pi - \Theta) V(\mathbf{r}', t) \psi_0(\mathbf{r}') \exp[2\pi i(W - W_0)t/h]. \quad (20)$$

Here $\cos \Theta = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi')$, (21)

and $\mathfrak{F}(r, \theta)$ is the function discussed in Chap. II, § 1, i.e.

$$\mathfrak{F}(r, \theta) = \sum_n (2n+1) i^n e^{i\eta_n} P_n(\cos \theta) L_n(r),$$

which has asymptotic form

$$\mathfrak{F} \sim e^{ikz} + r^{-1} e^{ikr} \times \text{function of } \theta.$$

The function $\mathfrak{F}(r', \pi - \Theta)$ thus represents a plane wave in the opposite direction to θ, ϕ together with an *outgoing* wave, and is thus *not* the complex conjugate of the wave function of the final state. It is only when the influence of the nucleus on \mathfrak{F} may be neglected (fast electrons, small atomic number, $2\pi Z e^2 / \hbar v \ll 1$), so that $\mathfrak{F}(r', \pi - \Theta)$ may be replaced by $\exp(-ik\mathbf{n} \cdot \mathbf{r}')$, that \mathfrak{F} may be considered as the complex conjugate of the final state.†

3. Transitions due to a perturbing function periodic in the time

We take for the perturbing potential

$$V(\mathbf{r}, t) = \lambda U(\mathbf{r}) e^{-2\pi i \nu t} + \lambda U^*(\mathbf{r}) e^{2\pi i \nu t}, \quad (22)$$

where U is a function of r but not of t , and λ is a parameter. Assuming

† See Chap. III, p. 49, note at end of § 2.

that the perturbed system is in the state 0 at time $t = 0$, then at time t the wave function is, from (13),

$$\sum_s a_s(t) \psi_s(\mathbf{r}) \exp(-2\pi i W_s t / \hbar) + \int a_W(t) \psi_W(\mathbf{r}) \exp(-2\pi i W t / \hbar) dW, \quad (23)$$

where

$$a_s = \frac{\exp[2\pi i (W_s - W_0 - \hbar\nu)t / \hbar] - 1}{W_s - W_0 - \hbar\nu} \lambda U_{s0} + \frac{\exp[2\pi i (W_s - W_0 + \hbar\nu)t / \hbar] - 1}{W_s - W_0 + \hbar\nu} \lambda U_{s0}^*, \quad (24)$$

and
$$U_{s0} = \int \psi_s^*(\mathbf{r}) U(\mathbf{r}) \psi_0(\mathbf{r}) d\tau, \quad (25)$$

with a similar expression for a_W .

In order to obtain results of physical significance in problems where V is periodic, one must take t , the time during which the perturbation acts, to be great in comparison with $1/\nu$. One requires the probability $P_s \Delta t$ per time Δt ($\Delta t \gg 1/\nu$) that the atom will be excited or ionized, in contradistinction to the problem considered in § 2.1, where the probability of excitation during a single event (collision) was required. Denoting by $P = \sum P_s$ the total probability per unit time of excitation or ionization, then the probability that after time t the atom is still in its normal state is e^{-Pt} . The perturbation method used (cf. § 2.1) to obtain (25) is only correct for values of t such that this probability is not very different from unity, i.e. if

$$Pt \ll 1. \quad (26)$$

However, if the perturbation is due to a light wave, P_s will be proportional to its intensity, i.e. to λ^2 , and in calculating P_s we may take λ as small as we please. Thus it is always possible to choose t so that (26) shall be satisfied, consistently with the inequality $t \gg 1/\nu$. The perturbation method thus gives accurate results for intensities of perturbing field such that P is proportional to λ^2 , which is the case for all light waves.

The method of interpretation depends on whether the final state is quantized or whether it lies in the range of continuous energy values. In the former case the transition probability $|a_s|^2$ does not increase with the time, unless ν is equal to ν_{s0} , where $\nu_{s0} = |W_s - W_0|/\hbar$; in this case it increases with the square of the time, as may easily be seen from (24). To obtain a result of physical significance one must assume that the perturbing field is not strictly monochromatic, but

consists of a large number of fields of different frequency in the neighbourhood of ν_{s0} , superimposed on one another. The transition probability is now obtained by integrating $|a_s|^2$ with respect to ν over the critical value ν_{s0} . We write in (22) $\lambda^2 = d\nu$. The second term in (24) clearly contributes nothing of importance (if $W_s > W_0$), and we obtain for the transition probability

$$\int \frac{2[1 - \cos\{2\pi(W_s - W_0 - h\nu)t/h\}]}{[W_s - W_0 - h\nu]^2} |U_{s0}|^2 d\nu.$$

As t becomes large, the main part of the integral comes from the neighbourhood of $\nu = \nu_{s0}$. The integral reduces to†

$$4\pi^2 |U_{s0}|^2 t/h^2. \quad (27)$$

The Einstein B coefficient (absorption coefficient) may be calculated in this way.‡

If the final state lies in the range of continuous energy values, we may use the method of § 2.1. Thus we consider that the perturbation acts during a finite interval of time T , where $\nu T \gg 1$, but $PT \ll 1$. Then, from (24), $|a_W(T)|^2 dW$ is the probability that the electron is ejected with energy between W , $W + dW$. This function has a strong maximum for $W = W_0 + h\nu$. The total number of electrons ejected with all energies is

$$\int |a_W(T)|^2 dW = \int \frac{2[1 - \cos\{2\pi(W - W_0 - h\nu)T/h\}]}{[W - W_0 - h\nu]^2} \lambda^2 |U_{W0}|^2 dW. \quad (28)$$

As $\nu T \rightarrow \infty$, practically all the integral comes from the neighbourhood of $W = W_0 + h\nu$, so that (28) may be replaced by§

$$4\pi^2 T |\lambda U_{W0}|^2/h, \quad W = W_0 + h\nu, \quad (29.1)$$

which is the required probability that the electron is ejected in the time T . Similarly, the number of electrons ejected into the solid angle $d\omega$ is, per unit time, from (18), (20),

$$\nu \left| \frac{2\pi m}{h^2} \int \mathfrak{F}(r', \pi - \Theta) \lambda U(r') \psi_0(r') d\tau' \right|^2 d\omega. \quad (29.2)$$

† We make use of the formula

$$\int_{-\infty}^{\infty} \frac{1 - \cos x}{x^2} dx = \pi.$$

‡ For further details the reader is referred to Mott and Sneddon, *Wave Mechanics and its Applications*, p. 255.

§ N.B.—The hyperbolic wave function used in the evaluation of U_{W0} is normalized as in eq. (12) of this chapter.

Bethe† has shown how to interpret the wave function (23) without using the expedient of a perturbation that acts only in the time interval $0 < t < T$. In formula (23), if \mathbf{r} be a point outside the atom, ψ_s vanishes and ψ_W may be replaced by its asymptotic form

$$\psi_W \sim 2(hv)^{-1/2} r^{-1} \sin(kr - \frac{1}{2}n\pi + \eta_n) S_n^u(\theta, \phi).$$

Using this expression for ψ_W , we shall show that, so long as $vt \gg 1$, the wave function (23) corresponds to an outgoing wave of finite amplitude for $r < vt$ and vanishing for $r > vt$.

For points \mathbf{r} outside the atom, we have from (23), (24)

$$\Psi(\mathbf{r}, t) \sim \sum_{n,u} S_n^u(\theta, \phi) e^{-2\pi i(W_0 + hv)t/h} \int \lambda U_{Wnu,0} \frac{1 - e^{-2\pi i(W - W_0 - hv)t/h}}{W - W_0 - hv} \times (kr)^{-1} N(W) \sin(kr - \frac{1}{2}n\pi + \eta_n) dW. \quad (30)$$

In this integral we make the substitution

$$2\pi(W - W_0)t/h = \zeta,$$

so that

$$k = 2\pi(2mW)^{1/2}/h = k_v + \zeta/vt + O(1/t^2).$$

Here W_v is written for $W_0 + hv$, k_v for $2\pi(2mW_v)^{1/2}/h$. If vt is large, the integrand in (30) has a strong maximum for $W = W_v$, and (30) can be replaced by

$$\Psi \sim \sum_{n,u} N(W_v) S_n^u \lambda U_{W_vnu,0} e^{-2\pi iW_v t/h} \int \frac{1 - e^{-i\zeta}}{\zeta} \frac{\sin(kr - \frac{1}{2}n\pi + \eta_n)}{kr} d\zeta. \quad (31)$$

The integral on the right is equal to

$$(2ikr)^{-1} e^{ikr - i\pi n\pi + i\eta_n} \int [e^{i\zeta r/vt} - e^{i\zeta(r/vt-1)}] \zeta^{-1} d\zeta - (2ikr)^{-1} e^{-ikr + i\pi n\pi - i\eta_n} \int [e^{-i\zeta r/vt} - e^{i\zeta(-r/vt-1)}] \zeta^{-1} d\zeta. \quad (32)$$

Now if A, B are real numbers,

$$\int_{-\infty}^{\infty} [e^{iA\zeta} - e^{iB\zeta}] \frac{d\zeta}{\zeta} = i \int_{-\infty}^{\infty} \left[\frac{\sin A\zeta}{\zeta} - \frac{\sin B\zeta}{\zeta} \right] d\zeta,$$

which is clearly equal to 0 if A, B have the same sign, and to $2\pi i$ if they have opposite signs. Hence the second integral in (32), which represents the ingoing wave, vanishes; the first integral vanishes if $r > vt$, and is equal to $2\pi i$ if $r < vt$. Hence for (31) we may write

$$\Psi \sim (2kr)^{-1} e^{ikr - 2\pi iW t/h} 2\pi N(W) \sum_{n,u} \exp(i\eta_n - \frac{1}{2}n\pi i) S_n^u(\theta, \phi) \lambda U_{Wnu,0} \quad (r < vt) \\ \sim 0 \quad (r > vt).$$

Formulae (29.1), (29.2) for the number of electrons ejected may easily be deduced.

† *Ann. der Phys.* 4 (1930), 443.

3.1. Ionization of a hydrogen atom by a light wave

If we take for the scalar and vector potentials of the light wave

$$\Phi = \phi(x, y, z)e^{-2\pi i\nu t} + \text{complex conjugate},$$

$$\mathbf{A} = \mathbf{a}(x, y, z)e^{-2\pi i\nu t} + \text{complex conjugate},$$

then we have for the perturbing term the operator

$$V(\mathbf{r}, t) = U(\mathbf{r})e^{-2\pi i\nu t} + \text{complex conjugate},$$

where

$$U(\mathbf{r}) = -\epsilon\phi + (\epsilon\hbar/2\pi imc)\mathbf{a} \cdot \text{grad} \quad (\text{Schrödinger})$$

$$= -\epsilon\phi - \epsilon\rho_1(\boldsymbol{\sigma} \cdot \mathbf{a}) \quad (\text{Dirac}).$$

For a plane-polarized wave along the z -axis one may take

$$\phi = 0, \quad a_x = ae^{iqz}, \quad a_y = a_z = 0.$$

Hence

$$U_{s0} = \frac{\epsilon\hbar a}{2\pi imc} \int \psi_s^* e^{iqz} \frac{\partial \psi_0}{\partial x} d\tau.$$

If the light wave has wave-length long compared with the radius of the atom, e^{iqz} may be replaced by unity.†

4. Transitions caused by a perturbation which is not a function of the time

The formulae of the preceding section are at once applicable, by putting $\nu = 0$. Since in § 3.1 transitions were possible only to states of energy $W_0 \pm \hbar\nu$, where W_0 is the initial energy, it follows that transitions are only now possible to states of energy W_0 . Energy is therefore conserved in such transitions, as may be seen from the physical nature of the processes involved.

4.1. Final and initial states unquantized. Scattering of a beam of electrons by a centre of force

We make use of formula (29.2). For ψ_0 we take a beam of electrons normalized so that one electron crosses unit area per unit time, so that

$$\psi_0 = v^{-1} \exp(ik\mathbf{n}_0 \cdot \mathbf{r}).$$

$U(r)$ is the potential energy of the electron in the field of the scattering centre. $\mathfrak{F}(\mathbf{r}', \pi - \Theta)$ reduces to $\exp(-ik\mathbf{n} \cdot \mathbf{r}')$, where \mathbf{n} is a unit vector in the direction θ, ϕ . Thus (29.2) reduces to

$$\left| \frac{2\pi m}{\hbar^2} \int \exp[ik(\mathbf{n}_0 - \mathbf{n}) \cdot \mathbf{r}'] U(\mathbf{r}') d\tau' \right|^2,$$

† For the application of these formulae to the calculation of the photoelectric effect cf. Sommerfeld, *Wave Mechanics*, p. 177, and Heitler, *The Theory of Radiation*, 2nd edition, p. 119.

which is the formula obtained by the first approximation of Born's method [Chap. VII, eq. (5)].

4.2. *Initial state quantized, final state unquantized*

We take for our example a non-relativistic theory of the internal conversion of γ -rays. We suppose an α -particle in the nucleus, coordinate \mathbf{R} , is in an excited state described by a wave function $\chi_i(\mathbf{R})$, and an electron in the atom in the normal state in the K level, described by a wave function $\psi_i(\mathbf{r})$. We require the probability per unit time that the α -particle jumps to its normal state (wave function $\chi_f(\mathbf{R})$), giving up its energy to the electron, which is thereby ejected. If

$$V(\mathbf{r}, \mathbf{R}) = -2e^2/|\mathbf{R} - \mathbf{r}|$$

be the interaction between them, then by (23) this probability is

$$\sum_s \frac{4\pi^2}{h} \left| \iint d\mathbf{r} d\mathbf{R} \chi_f^* \psi_f^* V(\mathbf{r}, \mathbf{R}) \chi_i \psi_i \right|^2 d\omega, \quad (33)$$

where ψ_f represents the wave function of the final state normalized as in equation (12), and the summation is over all possible final states with the requisite energy.

The escape of an α -particle from a radioactive nucleus has been treated by this method by Born.†

† *Zeits. f. Physik*, 58 (1929), 306.

RELATIVISTIC TWO-BODY PROBLEMS—RADIATION

It is not our intention in this chapter to discuss the various difficulties associated with the relations between quantum mechanics, electrodynamics, and the special theory of relativity. These are intimately bound up with the concept of, and technique for, dealing with radiative phenomena. In this book we restrict ourselves to the discussion of collision processes in which radiation, involving emission and absorption of particles, does not occur. We continue largely to maintain the discrimination in this chapter, which is mainly concerned with collisions between two particles under relativistic conditions. Nevertheless, we show briefly how the technique, which we have developed for dealing with non-radiative phenomena, may be applied also to radiative processes. The formulae obtained are identical with those normally used for such problems, derived by the method of variation of parameters, so reference may be made to standard works on radiation phenomena† for a discussion of the applications.

1. Relativistic quantum mechanics. Use of retarded potentials

The work of Dirac‡ provides a complete relativistic theory of the motion of a single particle (proton or electron) in an electromagnetic field. Dirac's theory has been applied to the hydrogen atom,§ to the nuclear scattering of fast electrons,|| and to the interaction of an electron with electromagnetic radiation of high frequency.†† On the other hand, a complete relativistic theory of problems involving the interaction of two or more particles is, at present, lacking. However, there is a certain limited class of such problems which may be solved; namely, the calculation of transition probabilities under conditions such that first-order perturbation theory (first Born approximation) is valid.

In order to illustrate the method by which such transition probabilities may be calculated, we shall consider the following problem (Auger effect). In a heavy atom a K electron has been ejected; there is therefore a finite probability that an L electron will fall into the K

† Heitler, *The Theory of Radiation*, 2nd edition, Oxford (1945).

‡ *Proc. Roy. Soc. A*, **117** (1928), 618, and *Quantum Mechanics*, 3rd edition, Chap. XI.

§ Darwin, *Proc. Roy. Soc.* **118** (1928), 654; Gordon, *Zeits. f. Physik*, **48** (1928), 1.

|| Cf. Chap. IV, § 4, of this book.

†† For the Compton effect cf. Klein and Nishina, *Zeits. f. Physik*, **52** (1929), 893, and Heitler, *The Theory of Radiation*, 2nd edition, Oxford (1945) p. 146; for photoelectric effect cf. Hulme, *Proc. Roy. Soc. A*, **133** (1931), 381; Sauter, *Ann. der Phys.* **9** (1931), 217; Heitler, loc. cit., p. 119.

ring, giving up its energy either to a light quantum or to one of the other atomic electrons. We shall calculate the probability that the L electron gives up its energy to an optical electron.

The method we shall use precludes the possibility of using anti-symmetrical wave functions for the initial or final states. We shall treat the electrons separately, denoting by \mathbf{R} the position of the inner electron, by $\chi_i(\mathbf{R})$ the wave function of its initial state in the L ring, and by $\chi_f(\mathbf{R})$ its final state in the K ring. We denote the wave function of the initial state of the optical electron by $\psi_i(\mathbf{r})$ and the final ionized state by $\psi_f(\mathbf{r})$. The effect of the antisymmetry is considered at the end of this section.

The inner electron can return to the K level either by giving up its energy to the electron, or by emitting a quantum of radiation. The probability per unit time of the latter event is denoted by $A_{i \rightarrow f}$, the Einstein A coefficient. According to any completely non-relativistic theory ($c \rightarrow \infty$) the A coefficient is zero, since in the absence of a radiation field the atom will stay in the excited state for ever. Dirac† has been able to account for the A coefficient by treating the radiation field as an assembly of light quanta obeying quantum-mechanical laws. Before the formulation of Dirac's theory the A coefficient was obtained in the following way.‡

The radiating system—in our case the L electron—is treated as a classical charge distribution, of density

$$\rho_{fi} \exp(-2\pi i\nu_{fi} t) + \text{complex conjugate}, \quad (1)$$

where

$$\rho_{fi} = -e\chi_f^* \chi_i.$$

The current vector corresponding to this charge density is

$$\mathbf{j}_{fi} \exp(-2\pi i\nu_{fi} t) + \text{complex conjugate},$$

where

$$\mathbf{j}_{fi} = e\chi_f^* \rho_1 \boldsymbol{\sigma} \chi_i, \quad (\text{Dirac's equation})$$

$$= \frac{e\hbar}{4\pi im} (\chi_f^* \text{grad } \chi_i - \chi_f \text{grad } \chi_i^*) \quad (\text{Schrödinger's equation}).$$

On the classical theory such a charge density will give rise to an oscillating electromagnetic field, radiating energy. The energy radiated per unit time may be calculated. If we divide this by the energy of a light quantum, $E_i - E_f$, we obtain a formula for the A coefficient.

It is clear that this method of calculating the A coefficient is an unsatisfactory mixture of classical and quantum mechanics; nevertheless

† *Proc. Roy. Soc. A*, **114** (1927), 243, and *Quantum Mechanics*, 3rd edition, p. 244.

‡ Cf. O. Klein, *Zeits. f. Physik*, **41** (1927), 407.

it is along these lines that we must proceed in order to obtain a relativistic theory of the interaction of two particles. We proceed to find the field due to the oscillating charge density (1).

By classical electromagnetic theory the scalar potential Φ and vector potential \mathbf{A} due to this charge density are given by the differential equations

$$\nabla^2\Phi - \frac{1}{c^2} \frac{\partial^2\Phi}{\partial t^2} = -4\pi\rho_{fi} \exp(-2\pi i\nu_{fi}t) + \dots, \tag{2.1}$$

$$\nabla^2\mathbf{A} - \frac{1}{c^2} \frac{\partial^2\mathbf{A}}{\partial t^2} = -\frac{4\pi}{c} \mathbf{j}_{fi} \exp(-2\pi i\nu_{fi}t) + \dots \tag{2.2}$$

To obtain a particular integral we set

$$\left. \begin{aligned} \Phi &= \phi(x, y, z) \exp(-2\pi i\nu_{fi}t) \\ \mathbf{A} &= \mathbf{a}(x, y, z) \exp(-2\pi i\nu_{fi}t) \end{aligned} \right\} + \text{complex conjugate}, \tag{3}$$

and obtain
$$(\nabla^2 + 4\pi^2\nu_{fi}^2/c^2)\phi = -4\pi\rho_{fi}, \tag{4}$$

etc. The solution of this equation, representing an outgoing wave only, is

$$\phi = \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} \exp(2\pi i\nu_{fi}|\mathbf{r}-\mathbf{r}'|/c) \rho_{fi}(x', y', z') d\tau'. \tag{5}$$

Taking the asymptotic form of (5), we obtain, for large r ,

$$\Phi \sim r^{-1} \exp\{2\pi i\nu_{fi}(r/c-t)\} \int \exp(-2\pi i\nu_{fi} \mathbf{n} \cdot \mathbf{r}'/c) \rho_{fi}(x', y', z') d\tau' + \dots,$$

where \mathbf{n} is the vector \mathbf{r}/r . A similar expression is obtained for the vector potential; the rate of emission of energy may thus be calculated.

In order to obtain the probability that the L electron will give up its energy to the optical electron, we proceed as though the field Φ, \mathbf{A} given by (5) were in fact present, and calculate its effect on the optical electron by the method of Chap. XIV, § 3. The probability of ejection increases with the time, only if the energy received by the electron is equal to $\pm h\nu_{fi}$. The probability per unit time is then (Chap. XIV, eq. (29.1))

$$\frac{4\pi^2}{h} \left| \int \psi_f^* \{-\epsilon\phi - \epsilon\rho_1 \mathbf{a} \cdot \boldsymbol{\sigma}\} \psi_i d\tau \right|^2, \tag{6}$$

where ψ_f is the wave function of the final state of the electron, normalized to represent one emitted electron per unit time.

If we make $c \rightarrow \infty$ in (5), we obtain

$$\begin{aligned} \phi &= -\epsilon \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} \chi_f^*(\mathbf{r}') \chi_i(\mathbf{r}') d\tau', \\ \mathbf{a} &= \mathbf{0}, \end{aligned}$$

and hence (6) reduces to the non-relativistic formula, Chap. XIV, eq. (33).

With this method of treatment it is meaningless to inquire whether the optical electron is ejected by direct interaction with the L electron, or whether a light quantum is first emitted and then re-absorbed. Both processes are included in (6).

Formula (6) takes no account of the antisymmetrical property in non-relativistic quantum mechanics. We can obtain a formula which, as $c \rightarrow \infty$, tends to the non-relativistic formula with antisymmetrical wave functions. Let us denote by $|A|^2$ the expression (6). $|A|^2$ is the probability that the L electron falls to the ground state, and the optical electron is ejected. Similarly we can find the probability $|B|^2$ that the optical electron falls to the ground state, and the L electron is ejected. The required expression is

$$|A - B|^2,$$

which is probably the correct expression for the number of electrons ejected of both kinds. The expression must be summed over all possible final states.

Calculations on these lines for the Auger effect have been carried out by Massey and Burhop,[†] to whose paper the reader may be referred for details.

2. Relativistic treatment of collision problems

The excitation and ionization of atoms by fast electrons may be treated by the method of § 1.[‡] We shall consider the problem of a beam of electrons incident on a hydrogen atom in the normal state, with wave function $\psi_i(\mathbf{r})\exp(-2\pi i E_i t/\hbar)$. We require the probability that an electron is scattered in a given direction after exciting the atom to a state with wave function $\psi_f(\mathbf{r})\exp(-2\pi i E_f t/\hbar)$.

As in § 1, the interaction between the two electrons is treated as a small perturbation. For the unperturbed wave function of the incident electrons one should take, therefore, the wave function for a stream of electrons scattered by a nucleus (Chap. III, eq. (23)). Since, however, $v \sim c$, $\epsilon^2/\hbar v \ll 1$, so that this may be replaced by a plane wave, to the order to which we are working [neglect of $(\epsilon^2/\hbar c)^2$, cf. § 3]. We therefore take for our zero-order wave function χ_i , a plane wave normalized to give one electron crossing unit area per unit time, so that

$$\chi_i(\mathbf{R}) = v^{-1} \exp\{2\pi i(p_z Z - Wt)/\hbar\}.$$

For the corresponding wave function with Dirac electrons, cf. Chap. IV, eq. (12).

[†] *Proc. Roy. Soc. A*, **153** (1936), 661.

[‡] The method is due to Møller, *Zeits. f. Physik*, **70** (1931), 786.

To obtain the probability of scattering we treat the atom as a varying charge distribution of density (cf. (1) above)

$$-\epsilon\psi_f^*(\mathbf{r})\psi_i(\mathbf{r})\exp\{2\pi i(E_f - E_i)t/\hbar\}, \quad (7)$$

with a corresponding expression for the current; we then calculate the effect of the field of this charge on the incident beam of electrons. The method is that of Chap. XIV, § 3. The theory predicts that electrons will be scattered with energies $W - E_f + E_i$. One must *not* add the complex conjugate term to (7), for this would predict the presence of electrons scattered with energy $W - E_i + E_f$, more energy than they had initially.†

The field due to (7) cannot be interpreted as the field radiated by the atom, as in § 1, firstly, because the atom is initially in its normal state and is not radiating, and secondly, because the field is complex.

With ϕ and \mathbf{a} given by § 1, equations (3) and (4), we see from Chap. XIV, eq. (29.2), that the differential cross-section for scattering in a solid angle $d\omega$ is

$$|f(\theta)|^2 d\omega = v_f \left| \frac{2\pi m}{\hbar^2} \int \mathfrak{F}(\mathbf{r}') [-\epsilon\phi - \epsilon\rho_1(\boldsymbol{\sigma} \cdot \mathbf{a})] \chi_i(\mathbf{r}') d\tau' \right|^2 d\omega, \quad (8)$$

where \mathfrak{F} is the complex conjugate of the wave function for an electron moving in the direction \mathbf{p}_f , normalized so that there is one particle per unit volume (i.e. for Schrödinger electrons $\mathfrak{F} = \exp(-2\pi i\mathbf{p}_f \cdot \mathbf{r}'/\hbar)$, for Dirac, cf. Chap. IV, eq. 12).

In the non-relativistic theory one must use an antisymmetrical wave function to describe a collision between an electron and a hydrogen atom. In the relativistic theory discussed here no wave function for the whole system appears, but we can take account of the antisymmetry in the same way as in § 1. Thus in equation (8) we have obtained an expression $|f(\theta)|^2 d\omega$ for the probability that an electron will be scattered into the solid angle $d\omega$. If in (7) we replace $\psi_f(\mathbf{r})$ by a hyperbolic wave function describing an electron ejected with momentum p_f , and \mathfrak{F} in (8) by the wave function $\psi_f(\mathbf{r})$ of an electron captured in the state f in the atom, we obtain the probability $|g(\theta)|^2 d\omega$ that the incident electron is captured, and the atomic electron ejected. In the non-relativistic theory, when one takes account of the antisymmetry, the probability for scattering into the solid angle $d\omega$ is

$$\sum |f(\theta) - g(\theta)|^2 d\omega, \quad (9)$$

† In the case of § 1 there is no final state of energy $W_i - E_i + E_f$. Thus the presence of the conjugate term makes no difference to the number of electrons ejected.

where the summation is over all possible initial and final directions of the spin (cf. Chap. V, § 6). We may assume that, in the relativistic theory also, the scattering is given by the formula (9).

Formulae for the stopping-power and primary ionization may be obtained by evaluating integrals of the type (8), and summing over all final states. (For results see below.) We must, however, remark here that all important contributions to the primary ionization are made by collisions in which the incident electron changes its momentum by a small amount only. Under these conditions the method of impact parameters is applicable. Williams† has shown that all the results given below may be deduced by this method, the incident electron being treated as a moving centre of force, with the field demanded by the ‘classical’ relativity theory. We conclude that an experimental test of these formulae does not provide a test of the relativistic quantum theory of the interaction of two electrons. This theory only provides formulae which can be obtained in no other way, when applied to problems where the incident particle loses a large proportion of its energy.

The formulae for the stopping-power and cross-section for ionization are,‡ in the notation of Chap. XI, §§ 3.3 and 4.2,

$$-\frac{dT}{dx} = \frac{2\pi\epsilon^4 N}{mv^2} \left\{ \log \frac{2mv^2}{\alpha R\hbar} - \log \left(1 - \frac{v^2}{c^2} \right) - \frac{v^2}{c^2} \right\},$$

$$Q_{nl}^i = \frac{2\pi\epsilon^4 c_{nl} Z_{nl}}{mv^2 |E_{nl}|} \left\{ \log \frac{2mv^2}{C_{nl}} - \log \left(1 - \frac{v^2}{c^2} \right) - \frac{v^2}{c^2} \right\}.$$

By comparison with the corresponding formulae (68) and (50) of Chapter XI we see that the chief difference between these relativistic formulae and the non-relativistic formula is the presence in the relativistic formulae of a term $-\log(1-v^2/c^2)$. This term has the effect of producing a minimum in dT/dx and Q_{nl}^i at sufficiently high velocities. Otherwise there is no appreciable modification. Thus for electrons in air Bethe and Fermi give the following values of dT/dx :

Initial energy in volts	10 ⁵	10 ⁶	10 ⁷	10 ⁸	10 ⁹	10 ¹⁰
dT/dx	3.67	1.69	1.95	2.47	2.99	3.48

Experimental verification of the formulae by use of cosmic ray electrons was delayed by the failure at first to distinguish between the meson and electron components of the radiation. The more recent

† *Proc. Roy. Soc.* **139** (1933), 163.

‡ These formulae have been derived by Bethe and Fermi, *Zeits. f. Physik*, **77** (1932), 296, using Møller’s method, and by E. J. Williams, loc. cit., using the method of impact parameters.

experiments of Corson and Brode† and of Hazen‡ have, however, provided confirmation.

It is important to remember, moreover, that for these high-energy particles a large part of the energy transfer occurs in very distant collisions. The perturbing influence of neighbouring atoms can then no longer be disregarded. This effect, first pointed out by Fermi,§ reduces the energy loss in condensed materials so that, after passing through a minimum M.e.V., dT/dx increases to a finite maximum and not indefinitely. For further details the reader is referred to the original papers.||

3. Collision between two free electrons

The first application of the method of § 2 to a collision problem was made by Møller,†† who applied it to the collision between two free particles. Since the effect of one electron on the other is treated as a first-order perturbation, the results are of an accuracy equal to that of the first approximation in Born's method. With an inverse square law field, $V = \pm e^2/r$, the successive approximations in Born's method correspond to an expansion‡‡ in powers of the constant $2\pi e^2/hv$. A relativistic correction is only of interest if $v \sim c$, and thus Møller's formula neglects $2\pi e^2/hc$ in comparison with unity. An attempt to find a more accurate formula cannot be made without taking into account the loss of energy by radiation, since if a particle moving with velocity comparable with c is scattered through a large angle, the probability that it will lose energy in the form of radiation is of order of magnitude§§ $2\pi e^2/hc$.

Møller's formula||| for the cross-section for scattering between angles $\theta, \theta + d\theta$ is

$$I(\theta) d\theta = 4\pi \left(\frac{e^2}{mv^2} \right)^2 \frac{\gamma + 1}{\gamma^2} dx \left[\frac{4}{(1-x^2)^2} - \frac{3}{1-x^2} + \frac{(\gamma-1)^2}{4\gamma^2} \left\{ 1 + \frac{4}{1-x^2} \right\} \right], \quad (10)$$

$$\text{where} \quad x = \cos \theta^* = \frac{2 - (\gamma + 3)\sin^2 \theta}{2 + (\gamma - 1)\sin^2 \theta}, \quad \gamma = \left(1 - \frac{v^2}{c^2} \right)^{-\frac{1}{2}}.$$

† *Phys. Rev.* **53** (1938), 773; Brode, *Rev. Mod. Phys.* **11** (1939), 222.

‡ *Phys. Rev.* **67** (1945), 269.

§ *Ibid.* **56** (1939), 1242.

|| Fermi, loc. cit.; *Phys. Rev.* **57** (1940), 485; Halpern and Hall, *ibid.* p. 459, and **73** (1948), 477; Hayward, *ibid.* **72** (1947), 937; Hereford, **74** (1948), 574.

†† *Zeits. f. Physik*, **70** (1931), 786; *Ann. der Phys.* **14** (1932), 531.

‡‡ If we take for our unit of length $\hbar/2\pi mv$, Schrödinger's equation for an electron in the inverse square law field becomes

$$\nabla^2 \psi + (1 \pm 4\pi e^2/hvr)\psi = 0.$$

Dirac's second-order equation takes a similar form (cf. Mott, *Proc. Roy. Soc. A*, **124** (1931), 425).

§§ Cf. § 9. If the two colliding particles are of equal mass and charge, the dipole moment vanishes and the probability of radiation is much less.

||| *Ann. der Phys.* **14** (1932), 568, eq. (74).

θ^* is the angle of scattering referred to axes with respect to which the centre of gravity of the two electrons is at rest. It is interesting that if one applies the method of the preceding sections, using the second-order relativistic wave equation without the spin terms, one obtains the same formula without the term

$$\frac{(\gamma-1)^2}{4\gamma^2} \left[1 + \frac{4}{1-x^2} \right], \tag{11}$$

which may thus be considered as the contribution made by the spin.

For small angles Møller's formula gives for the effective cross-section for loss of energy between Q , $Q+dQ$

$$\frac{2\pi\epsilon^4}{mv^2} \frac{dQ}{Q^2}, \tag{12}$$

a result predicted by Bohr† in 1913.

Experiments have been carried out by Champion‡ to test the formula (10). Two hundred and fifty forked β -ray tracks have been photographed in an expansion chamber, the initial values of v/c lying between 0.82 and 0.92. The agreement with the theoretical formula is good, as shown below.

Angle	No. scattered	
	Obs.	Møller
30-max.	10	13
20-30	26	30
10-20	214	230

It should, however, be noticed that the 'spin' term (11) makes only a very small contribution for angles less than 30° .

On the other hand, Williams and Terroux§ and Williams|| have produced evidence which shows that, for $v/c \sim 0.9$ and $Q \sim 10,000$ volts, the energy loss is about twice as great as that given by formula (12).

4. Pair production by fast particles

In Chap. IV, § 5, Dirac's theory of the positron and its consequences, as far as the creation and annihilation of electron-positron pairs are concerned, was discussed. A fast particle with energy $> 2\mu c^2$, passing a nucleus or other scatterer, may excite an electron from one of the states of negative mass to a state in which the mass is positive. This

† *Phil. Mag.* **25** (1913), 10; **30** (1915), 58.

‡ *Proc. Roy. Soc. A*, **137** (1932), 688.

|| *Ibid.* **130** (1930), 328.

§ *Ibid.* **126** (1929), 289.

process, which will appear as the creation of an electron and a positron (the hole in the distribution of electrons of negative mass), is essentially similar to an inelastic collision in which the initial state of the 'bound' electron is one of the negative mass continuum. Formula (8) may therefore be used to give the cross-section with the functions $\psi_i(\mathbf{r})$, $\psi_f(\mathbf{r})$ of (7) representing respectively an electron in the initial negative mass state and in the final state of positive mass. If \mathbf{p}_- , \mathbf{p}_+ are the momenta of the created positron and electron, then ψ_i is a Dirac wave function for an electron of momentum $-\mathbf{p}_+$ and kinetic energy $-(p_+^2 c^2 + m^2 c^4)^{\frac{1}{2}}$ in the field of the scattering nucleus, ψ_f the corresponding function for momentum \mathbf{p}_- and kinetic energy $(p_-^2 c^2 + m^2 c^4)^{\frac{1}{2}}$. This will be valid provided the interaction of the incident particle and the electron with each other is much weaker than either with the scatterer.

To obtain a finite cross-section, the functions $\mathfrak{F}(\mathbf{r}')$, $\chi_i(\mathbf{r}')$, ψ_i , ψ_f cannot be all represented by plane waves. Momentum can only be conserved if there is some interchange with the scattering nucleus, i.e. some disturbance of the waves by the scattering field. In the first non-vanishing approximation the functions may be represented by the second Born approximation, i.e. in the non-relativistic limit by

$$\mathfrak{F}(\mathbf{r}) = \exp\{-i\mathbf{p}_f \cdot \mathbf{r}/\hbar\} + \frac{2\pi m}{\hbar^2} \int \exp\left\{-\frac{i}{\hbar}(p_f |\mathbf{r}-\mathbf{r}'| + \mathbf{p}_f \cdot \mathbf{r}')\right\} \frac{V(r')}{|\mathbf{r}-\mathbf{r}'|} d\tau', \quad (13)$$

$V(r')$ being the potential energy due to the scatterer, with similar expressions for the other functions.

The detailed evaluation of the cross-section involves very lengthy algebra and has not been carried through in general. The most detailed calculations are due to Bhabha.† For creation, by collision with a bare nucleus (charge $Z\epsilon$), of electrons so fast that $\gamma = (1-\beta^2)^{-\frac{1}{2}} \gg 1$, the cross-section is given approximately by

$$Q = \frac{28}{27\pi} \left(\frac{Z}{137}\right)^2 \left(\frac{\epsilon^2}{mc^2}\right)^2 \{\log(\alpha\gamma)\}^3, \quad (14)$$

where α is a quantity of order unity. Table I gives some values for Q and also for the ratio Q/Q_γ , where Q_γ is the cross-section for pair production by γ -rays of the same quantum energy as the total energy of the electron.‡ Provided $\gamma \gg 1$ the values given hold also for creation by protons with the same value of γ as the electrons.

† *Proc. Roy. Soc. A*, **152** (1935), 559.

‡ Heitler, *The Theory of Radiation*, 2nd edition, Oxford (1945), Chap. IV.

TABLE I
Cross-Sections Q in 10^{-24} cm.² for the Creation of Pairs in Lead by Fast Particles

γ		10	50	100	500	1,000
Particle energy M.e.V. } Electrons		5	25	50	250	500
	Protons	8,500	46,000	93,000	470,000	940,000
Q		0.11	0.56	0.9	2.2	2.9
Q/Q_γ		0.004	0.01	0.02	0.05	0.06

Q_γ is the cross-section for creation of pairs by γ -rays of the same quantum energy as the electrons.

5. Radiationless annihilation of positrons

A positron colliding with an atom presents a vacant state into which an atomic electron may fall, releasing energy $> 2mc^2$. This may either be radiated or given to a second electron which then leaves the atom with high kinetic energy. In this way a positron will be annihilated without emitting radiation.

The process is essentially an Auger effect and (6) may be applied, the function χ_f being the Dirac wave function for an electron of momentum $-\mathbf{p}_+$ and energy $-(p_+^2 c^2 + m^2 c^4)^{\frac{1}{2}}$, \mathbf{p}_+ being the momentum of the positron.

The probability of this process is rather low (in lead about one in 10^4 of all positrons would be annihilated in this way). A detailed discussion is given in a paper by Massey and Burhop.†

6. Collision of a positron and a free electron

If exchange is neglected Møller's formula (10) reduces to

$$4\pi \left(\frac{e^2}{mv^2} \right)^2 \frac{\gamma+1}{\gamma^3} dx \left\{ \frac{4}{(1-x)^2} - \frac{2(\gamma^2-1)}{\gamma} (1-x) + \frac{(\gamma-1)^2}{2\gamma} (1-x)^2 \right\}. \quad (15)$$

At first sight one would expect this formula to be valid for the collision of positrons with electrons as, being different particles, there should be no exchange effects. It was pointed out by Bhabha,‡ however, that according to the hole theory of the positron an exchange effect would be expected. This arises in the following way.

Initially the electron occupies a positive mass state a_i and the positron represents a vacant negative mass state b_i . After the collision the corresponding states are a_f, b_f . The collision can be regarded then as an impact between the electron 1 in state a_i with an electron 2, of negative

† *Proc. Roy. Soc. A*, **167** (1938), 53.

‡ *Ibid.* **A**, **154** (1936), 195.

mass, in the state b , as a result of which, either electron 1 jumps to a , and 2 to b_i or 2 to a , and 1 to b_i . The exchange effect is due to the latter possibility. Alternatively it can be regarded as due to the mutual annihilation of the colliding electron and positron, followed by their re-creation in a different pair of states.

As a result of this effect the formula (15) is modified to give

$$4\pi \left(\frac{\epsilon^2}{mv^2} \right)^2 \frac{\gamma+1}{\gamma^3} dx \left[\frac{4}{(1-x)^2} - 2 \frac{\gamma-1}{\gamma+1} (2\gamma^2+4\gamma+1) \frac{1}{1-x} + \frac{1}{2} (\gamma-1)^2 \times \right. \\ \left. \times \left\{ 5 + \left(\frac{\gamma-1}{\gamma+1} \right)^2 (\gamma^2+2\gamma+3) - \gamma \left(\frac{\gamma-1}{\gamma+1} \right)^3 \right\} (1-x) + \frac{1}{4} \left(\frac{\gamma-1}{\gamma+1} \right)^4 (1-x)^2 \right]. \quad (16)$$

Unlike the collision of two electrons, in this case the effect of exchange vanishes in the non-relativistic limit $\gamma \rightarrow 1$, as would be expected from its nature.

The difference between (15) and (16) is most marked at large scattering angles, but is never greater than a factor of 2. Quite accurate experiments will be necessary to confirm the existence of the exchange effect, although preliminary measurements have been made by Ho Zah-Wei.†

7. Collision of a meson with an electron

The collision of a fast meson with an electron can be discussed by means of the formula (6), the potentials ϕ and \mathbf{a} being those corresponding to the initial and final states of the meson. The result depends on the spin of the meson, as a considerable contribution can come from the interaction of this spin with the orbital motion and with the electron spin.

For practical purposes it is convenient to give the cross-section $S(Q) dQ$ for energy loss between Q and $Q+dQ$ by the meson, Q being measured in units of μc^2 , where μ is the meson mass. We then find‡

$$S(Q) dQ = 2\pi \left(\frac{\epsilon^2}{mc^2} \right)^2 \alpha \frac{dQ}{Q^2} \left[\frac{\gamma^2}{\gamma^2-1} - \frac{Q}{Q_m} + G(Q) \right], \quad (17)$$

where

$$G(Q) = 0, \quad \text{for mesons with spin } 0, \quad (18)$$

$$= \frac{Q^2}{2(\gamma^2-1)}, \quad \text{for mesons with spin } \frac{1}{2}, \quad (19)$$

$$= \alpha \left(\frac{2\gamma^2+1}{6(\gamma^2-1)} \right) Q + \left(\frac{1}{\gamma^2-1} - \frac{\alpha}{Q_m} \right) \frac{1}{3} Q^2 + \frac{\alpha Q^3}{6(\gamma^2-1)}, \quad \text{for mesons with spin } 1. \quad (20)$$

† *Comptes Rend.* **222** (1946), 1168.

‡ Massey and Corben, *Proc. Camb. Phil. Soc.* **35** (1939), 463; Corben and Schwinger, *Phys. Rev.* **58** (1940), 953; Bhabha, *Proc. Roy. Soc. A*, **164** (1938), 257.

In these formulae $\alpha = m/\mu$ and Q_m , the maximum value of Q , is given by

$$Q_m = \frac{2\alpha(\gamma^2 - 1)}{1 + 2\alpha\gamma + \gamma^2}.$$

The most interesting case is that of the meson of spin 1, first discussed by Massey and Corben.† In the extreme relativistic limit, when $\alpha Q \gg 1$, $S(Q)$ is $\frac{1}{3}\alpha Q$ times as large for vector mesons (spin 1) as for mesons with spin $\frac{1}{2}$. This would result in a considerable excess of fast projected electrons due to meson impact at very high energies. The production of showers by the meson (penetrating) component of cosmic rays is probably due in the first instance to production, either of such electrons, or of high-energy quanta by ‘bremstrahlung’ from the meson in passing a nucleus. At first the latter effect was neglected and it was then found‡ that the probability of production by the penetrating component was in agreement with the observations, if formula (20) was used to give the rate of production of fast knock-on electrons. This was taken to indicate that mesons have spin 1, but it was found§ that the neglected effect was more important than the one considered and it now seems that the evidence,|| though far from definite, favours the assignment of a spin less than unity to the mesons observed near sea-level.

An important question arises also as to whether Møller’s method breaks down when the spin effects are so large. To investigate this point it is natural to consider the scattering of vector mesons by a static Coulomb field without resort to approximation.

8. Scattering of vector mesons by a static field

For the scattering by a static Coulomb field of charge $Z\epsilon$, Born’s approximation gives a result which may be obtained from the case discussed in the preceding section by letting $\alpha \rightarrow 0$. The differential cross-section is given by

$$I(\theta) = \frac{Z^2\epsilon^4}{4\mu^2v^4} \frac{1}{\gamma^2} \operatorname{cosec}^4 \frac{1}{2}\theta \left\{ 1 + \frac{(\gamma^2 - 1)^2}{6\gamma^2} \sin^2\theta \right\}. \quad (21)$$

This may be compared with the corresponding result (Chap. IV, § 4.2)

† Loc. cit.

‡ Bhabha, Carmichael, and Chou, *Proc. Ind. Acad. Sci.* **10** (1939), 221; Carmichael and Chou, *Nature*, **144** (1939), 325.

§ Christy and Kusaka, *Phys. Rev.* **59** (1941), 414; Booth and Wilson, *Proc. Roy. Soc. A*, **175** (1940), 483.

|| Christy and Kusaka, loc. cit.; Kusaka, *Phys. Rev.* **64** (1943), 256; Majumdar, *ibid.* **6** (1944), 206.

for a particle of spin $\frac{1}{2}$ in which the expression in brackets is replaced by

$$1 - \frac{\gamma^2 - 1}{\gamma^2} \sin^2 \theta.$$

Whereas in the latter case the spin contributes a term which remains finite in the limit $v \rightarrow c$, the effect of spin, for a vector or pseudo-vector meson, increases without limit as $v \rightarrow c$.

Doubt as to the validity of this result is enhanced by consideration of the scattering problem without use of the Born approximation. This was first done by Corben and Schwinger† and by Tamm‡ using the Proca equations for the vector meson. It is possible to separate the radial and angular coordinates. For a given total angular momentum $\{j(j+1)\}^{\frac{1}{2}}\hbar$, the radial motion of the mesons with $j = l$, where $\{l(l+1)\}^{\frac{1}{2}}\hbar$ is the orbital angular momentum, is described by the usual Klein-Gordon equation for a particle of spin 0 and mass μ . For mesons with $l = j \pm 1$ the radial motion is coupled as two second-order simultaneous equations. It is found then that, for a Coulomb field, these latter equations include an essential singularity at the origin which prevents one from obtaining the complete set of proper solutions necessary for the scattering problem. It is not yet clear to what extent the scattering does depend on the way the singularity is removed. Until this is decided the validity of the formula (21) and also of (20) must remain in doubt.

A detailed formal treatment of the scattering of vector mesons by a static field of potential $V(r)$ has been given by Gunn,§ in terms of the asymptotic phases of the different partial waves, on the assumption that proper solutions exist. The expressions obtained are natural generalizations of those given in Chap. V, § 4, for the scattering of Dirac electrons.

9. Derivation of radiation formulae by Born's collision method

We show now how the method described in Chap. VIII, §§ 3 and 4, which has been applied to various phenomena involving collisions between systems in which no radiation is emitted, may also be employed to deal with radiative phenomena. In general it is less convenient for this purpose than methods such as those outlined in Chapter XIV, but it does, of course, lead to equivalent final formulae.

The possibility that a particle may emit radiation in a collision can be regarded formally as due to a coupling between the particle and the radiation field. This field may be represented by a distribution of

† *Phys. Rev.* **58** (1940), 953.

‡ *Ibid.* p. 952.

§ *Proc. Roy. Soc. A*, **193** (1948), 559; see also Bartlett, *Phys. Rev.* **72** (1947), 219.

harmonic oscillators quantized in the usual way. Radiation of a quanta of frequency ν is then due to an excitation of an oscillator with that frequency from the ground to the first excited state, due to the coupling.

We consider the radiation within an enclosure of large volume V . The number of quanta with frequency between ν and $\nu+d\nu$ is then given by

$$dN = \frac{8\pi}{c^3} V \nu^2 d\nu. \quad (22)$$

The vector potential associated with radiation of frequency ν_s can be written

$$\mathbf{A}_s(\mathbf{r}, t) = \mathbf{a}_s u_s(t) \sin\left\{\frac{2\pi\nu_s}{c} \boldsymbol{\alpha}_s \cdot \mathbf{r} + \beta_s\right\}, \quad (23)$$

where $\mathbf{a}_s, \boldsymbol{\alpha}_s$ are two perpendicular unit vectors and β_s is a phase angle. The time-variable amplitude factor $u_s(t)$ may be derived from a Hamiltonian†

$$H_{1s} = \frac{1}{2} p_s^2 + 2\pi^2 \nu_s^2 q_s^2, \quad (24)$$

where

$$u_s = \left(\frac{8\pi c^2}{V}\right)^{\frac{1}{2}} q_s, \quad \dot{u}_s = \left(\frac{8\pi c^2}{V}\right)^{\frac{1}{2}} p_s. \quad (25)$$

This may be used as a basis for quantization, the Hamiltonian for the radiation having the form

$$H_1 = \sum_s H_{1s}.$$

The corresponding wave equation

$$(H_1 - E)\psi = 0 \quad (26)$$

will have the proper solutions

$$\psi_{n_1 n_2 \dots n_s \dots} = \phi_{n_1}(q_1) \phi_{n_2}(q_2) \dots \phi_{n_s}(q_s) \dots, \quad (27)$$

where $\phi_{n_s}(q_s)$ is the proper solution of the harmonic oscillator equation with frequency ν_s and with the energy

$$E_{n_s} = (n_s + \frac{1}{2}) h \nu_s. \quad (28)$$

A state represented by the function (27) is thus one in which there are present n_s quanta of frequency ν_s .

In the presence of matter we may write the complete Hamiltonian in the form

$$H = H_1 + H_2 + H_3, \quad (29)$$

where H_2 is the Hamiltonian for the material particles, including the static interactions between them. H_3 represents the interaction between the matter and radiation. To obtain it we note that, under non-relativistic conditions, if p_i is the momentum, e_i the charge, and m_i the

† Fermi, *Rev. Mod. Phys.* 4 (1932), 131.

mass of the i th particle, the interaction is given by

$$\sum_i \left\{ -\frac{\epsilon_i}{m_i c} \mathbf{A} \cdot \mathbf{p}_i + \frac{\epsilon_i^2 A^2}{2m_i^2 c^2} \right\}. \tag{30}$$

We may therefore write

$$H_3 = -\left(\frac{8\pi}{V}\right)^{\frac{1}{2}} \sum_i \sum_s \frac{\epsilon_i}{m_i} \mathbf{a}_s \cdot \mathbf{p}_i q_s \sin \gamma_s + \frac{4\pi}{V} \sum_i \sum_s \sum_r \frac{\epsilon_i^2}{m_i} \mathbf{a}_s \cdot \mathbf{a}_r q_s q_r \sin \gamma_s \sin \gamma_r, \tag{31}$$

where
$$\gamma_s = \frac{2\pi\nu_s}{c}(\boldsymbol{\alpha}_s \cdot \mathbf{r}) + \beta_s. \tag{32}$$

Let us now consider, by way of illustration, the probability that a particle of mass m should, when scattered by a static potential $V(r)$, emit a quantum of radiation.

We denote by
$$I(\theta, \phi; \alpha, \beta; \nu) d\omega d\Omega d\nu \tag{33}$$

the probability that the particle will be scattered in the direction θ, ϕ into the solid angle $d\omega$ after emitting a light quantum of frequency between ν and $\nu + d\nu$ with its electric vector lying in the solid angle $d\Omega$ and in the direction α, β .

The Schrödinger equation may be written

$$\left[-\frac{\hbar^2}{8\pi^2m} \nabla^2 + V(r) + H_1(p_s, q_s) + H_3(q_s, \mathbf{r}, \mathbf{p}) - E \right] \Psi = 0. \tag{34}$$

We may now employ immediately formula (32) of Chapter VII with the following substitutions:

For $V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)$, $V(r) - H_3(q_s, \mathbf{r}, \mathbf{p})$.

ψ_0 , $\phi_{n_1}(q_1)\phi_{n_2}(q_2)\dots\phi_{n_s}(q_s)\dots$, (corresponding to $n_1, n_2, \dots, n_s, \dots$ quanta of frequency $\nu_1, \nu_2, \dots, \nu_s, \dots$ initially present).

ψ_n , $\phi_{n_1}(q_1)\phi_{n_2}(q_2)\dots\phi_{n_{s+1}}(q_{s+1})\dots$, (corresponding to $n_1, n_2, \dots, n_{s+1}, \dots$ quanta of frequency $\nu_1, \nu_2, \dots, \nu_s, \dots$ finally present).

$$d\tau_a d\tau_b, \prod_s dq_s. \tag{35}$$

The functions F_0, \mathfrak{F}_n will satisfy the equations

$$\left[\nabla^2 + k_{0,n}^2 - \frac{8\pi^2m}{\hbar^2} V \right] F_0, \mathfrak{F}_n = 0, \tag{36}$$

since, in this case

$$\begin{aligned} V_{00} &= \int [V(r) - H_3(q_s, \mathbf{r}, \mathbf{p})] |\phi_{n_1}|^2 |\phi_{n_2}|^2 \dots |\phi_{n_s}|^2 \dots dq_1 dq_2 \dots dq_s \dots, \\ &= V(r), \\ &= V_{nn}. \end{aligned} \quad (37)$$

Also, using the well-known result for the wave functions of the oscillator, that

$$\int_{-\infty}^{\infty} q_s \phi_{n_s}(q_s) \phi_{n_{s+1}}^*(q_s) dq_s = \left\{ \frac{(n_s + 1)h}{8\pi^2\nu} \right\}^{\frac{1}{2}}, \quad (38)$$

we have

$$\begin{aligned} V_{0n}(r) &= \int [V(r) - H_3(q_s, \mathbf{r}, \mathbf{p})] \phi_{n_s}(q_s) \phi_{n_{s+1}}^*(q_s) dq_s, \\ &= \left\{ \frac{(n_s + 1)h}{8\pi^2\nu} \right\}^{\frac{1}{2}} \frac{i\hbar\epsilon}{m} \left(\frac{8\pi}{V} \right)^{\frac{1}{2}} \sin \gamma_s \mathbf{a}_s \cdot \text{grad}. \end{aligned} \quad (39)$$

The contribution to $I(\theta, \phi; \alpha, \beta; \nu)$ from each oscillator of frequency ν_s may now be written down. As there are $8\pi V \nu_s^2 d\nu_s/c^3$ such oscillators we have, taking $n_s = 0$,

$$\begin{aligned} I(\theta, \phi; \alpha, \beta; \nu) d\nu &= \frac{8\nu\epsilon^2}{hc^3} \frac{k_n}{k} A \left| \int \mathfrak{F}_n(r', \pi - \Theta) \mathbf{a}_s \sin \gamma_s \cdot \text{grad} F_0(r', \theta') d\tau' \right|^2 d\nu, \end{aligned} \quad (40)$$

A indicating that an average over the phases β_s is to be taken.

To reduce this to a more familiar form, we note first that the region over which the product of F_0 and \mathfrak{F}_n is likely to contribute appreciably to the integral will not be greater than the initial or final wave-length of the particle. This will normally be much shorter than the wave-length of the emitted radiation, so that γ_s may be taken as constant over the region of importance. The average over the phases β_s then simply involves multiplication by $\frac{1}{2}$ and removal of the term $\sin \gamma_s$.

If we assume that the product $F_0 \mathfrak{F}_n$ vanishes faster than r^{-2} over the infinite sphere, we have, integrating by parts,

$$\begin{aligned} \int \mathfrak{F}_n \text{grad} F_0 d\tau &= \frac{1}{2} \int (\mathfrak{F}_n \text{grad} F_0 - F_0 \text{grad} \mathfrak{F}_n) d\tau, \\ &= \frac{1}{2} \int \mathbf{r} (\mathfrak{F}_n \nabla^2 F_0 - F_0 \nabla^2 \mathfrak{F}_n) d\tau. \end{aligned} \quad (41)$$

Using the equations (36) for F_0 and \mathfrak{F}_n we finally have, since

$$\begin{aligned} k^2 - k_n^2 &= 8\pi^2 m\nu/h, \\ \int \mathfrak{F}_n \text{grad} F_0 d\tau &= \frac{4\pi^2 m\nu}{h} \int \mathbf{r} \mathfrak{F}_n F_0 d\tau. \end{aligned} \quad (42)$$

In the scattering problem as specified, the product $F_0 \mathfrak{F}_n$ does not vanish faster than r^{-2} over the infinite sphere, but the same procedure may be adopted if we introduce a convergence factor $e^{-\lambda r}$ into the integrand and make λ tend to zero after integration.

We find then

$$I(\theta, \phi; \alpha, \beta; \nu) d\nu = \frac{64\pi^4 m^2 \nu^3}{h^4 c^3} \frac{k_n}{k} \left| \mathbf{a}_s \cdot \lim_{\lambda \rightarrow 0} \int \mathbf{r}' e^{-\lambda r'} \mathfrak{F}_n(r', \pi - \Theta) F_0(r', \theta') d\tau' \right|^2 d\nu. \quad (43)$$

If we integrate over all directions of emission and of polarization of the emitted quantum, we obtain

$$I(\theta, \phi; \nu) d\nu = \frac{128\pi^5 m^2 \nu^3}{3h^3 c^3} \left\{ \frac{1}{2} |M_x|^2 + \frac{1}{2} |M_y|^2 + |M_z|^2 \right\} d\nu, \quad (44)$$

where

$$\begin{aligned} M_x &= \lim_{\lambda \rightarrow 0} \int \frac{x'}{z'} y' e^{-\lambda r'} \mathfrak{F}_n(r', \pi - \Theta) F_0(r', \theta') d\tau'. \\ M_y &= \lim_{\lambda \rightarrow 0} \int \frac{y'}{z'} y' e^{-\lambda r'} \mathfrak{F}_n(r', \pi - \Theta) F_0(r', \theta') d\tau'. \\ M_z &= \lim_{\lambda \rightarrow 0} \int \frac{z'}{z'} y' e^{-\lambda r'} \mathfrak{F}_n(r', \pi - \Theta) F_0(r', \theta') d\tau'. \end{aligned} \quad (45)$$

This is the usual formula, used, for example, by Sommerfeld,† Scherzer,‡ and Maue§ in their investigation of the intensity of the continuous X-ray spectrum.

If the incident and scattered particles are fast, but not so fast that relativistic effects need be included, then Born's method (Chap. VII, § 1) may be used to give, in the second approximation,

$$F_0 \simeq \exp(ik\mathbf{n}_0 \cdot \mathbf{r}) - \frac{2\pi m}{h^2} \int V(r') \frac{\exp\{ik|\mathbf{r} - \mathbf{r}'|\}}{|\mathbf{r} - \mathbf{r}'|} \exp(ikz') d\tau', \quad (46)$$

with a similar expression for \mathfrak{F}_n with k, \mathbf{n}_0 replaced by k_n, \mathbf{n} . The second approximation must be included in order to give a finite result.

A similar procedure may be employed for other radiative problems. The process can be classified as of first, second, or higher order according as the first, second, or higher terms in the successive Born approximations must be included in order to obtain a finite result. In this way it may be shown that the method is completely equivalent to that normally used, which is based on the Dirac method of variation of parameters for dealing with time-dependent perturbations. A complete account of this method and its applications has been given by Heitler, to whose book|| the reader is referred for further information.

† *Ann. der Phys.* **11** (1931), 257.

‡ *Ibid.* **13** (1932), 137.

|| *The Theory of Radiation*, 2nd edition, Oxford (1945).

§ *Ibid.* p. 161.

10. Influence of radiative forces on nuclear scattering

If we apply (44), (45), and (46) to scattering of an electron by a Coulomb field ($V(r) = -Z\epsilon^2/r$) the differential cross-section for scattering of the electron into a given element $d\omega$ of solid angle with emission of a quantum of frequency between ν and $\nu + d\nu$ is given by†

$$I(\theta, \phi; \nu) d\nu d\omega = \frac{p'}{p} \frac{4\epsilon^2}{3hc} \frac{|\mathbf{p}' - \mathbf{p}|^2}{m^2 c^2} \frac{d\nu}{\nu} I_0(\theta, \phi) d\omega, \quad (47)$$

where

$$I_0(\theta, \phi) = \frac{Z^2 \epsilon^4}{4m^2 \nu^4} \operatorname{cosec}^4 \frac{1}{2} \theta$$

is the differential cross-section for elastic scattering, p and p' are the initial and final momenta of the electron.

It will be seen that a logarithmic divergence of the cross-section (47) appears if we integrate to zero frequency. This difficulty was first analysed by Bloch and Nordsieck.‡ They pointed out that, for low frequencies, the perturbation treatment outlined in the preceding section is quite invalid. In that treatment the coupling between the electron and the radiation is assumed small. It represents an expansion in powers of $\frac{\epsilon^2}{hc} \frac{v^2}{c^2} \log\left(\frac{E}{h\nu}\right)$, where E is the electron energy, which clearly breaks down for small ν . For such cases Bloch and Nordsieck developed a method in which the coupling between electron and radiation field is not treated as small but the scattering field is treated as a perturbation. In this treatment, which was extended by Pauli and Fierz,§ the logarithmic divergence for small ν no longer appears but in its place a divergence is introduced in the limit of very high frequencies.

The origin of this divergence has been investigated by Braunbek and Weinmann.|| The next approximation to that which gives (47) leads to a correction to the elastic scattering due to the radiation field. This can be regarded as due to the emission and reabsorption of virtual quanta by the electron in the presence of the nucleus. The correction to $I_0(\theta, \phi)$ due to virtual quanta with frequency between ν and $\nu + d\nu$ is found to be

$$\delta I_0(\theta, \phi) = -\frac{4\epsilon^2}{3hc} \frac{|\mathbf{p}' - \mathbf{p}|^2}{m^2 c^2} \frac{d\nu}{\nu} I_0(\theta, \phi). \quad (48)$$

In the limit of zero frequency this cancels the divergence in (47). On the other hand, as the quanta involved are virtual, there is no upper

† Mott, *Proc. Camb. Phil. Soc.* **27** (1931), 255.

‡ *Phys. Rev.* **52** (1937), 54.

|| *Zeits. Phys.* **110** (1938), 360.

§ *Nuovo Cim.* **15** (1938), 167.

limit to ν and the correction diverges as $\nu \rightarrow \infty$. It might be objected that relativistic considerations would modify (48) at high frequencies and it has indeed been shown by Dancoff† that, with a relativistic theory, the divergence is removed for particles of spin zero. This result has been extended to electrons by Lewis‡ who showed that the apparently divergent terms found by Dancoff for this case are due to the infinite electromagnetic mass, and can be eliminated by a mass renormalization. The correction δI_0 to the elastic cross-section is found to be negligibly small, i.e. for non-relativistic conditions

$$\frac{\delta I_0}{I_0} = -\frac{4\epsilon^2}{3hc} \frac{|\mathbf{p}' - \mathbf{p}|^2}{m^2 c^2} \log \frac{kmc^2}{E},$$

where k is $O(1)$ and E is the initial kinetic energy of the electron. Developments in quantum electrodynamics by Schwinger§ have yielded further cases in which finite reactive effects of radiation interaction can be separated from divergent contributions associated with infinite self-energy.

† *Phys. Rev.* **55** (1939), 959.

‡ Lewis, *Phys. Rev.* **73** (1948), 173.

§ Schwinger, *Phys. Rev.* **74** (1948), 1439.

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